Journal of
Inorganic & Nuclear Chemistry

VOLUME 25 1963

EDITORS

JOSEPH J KATZ, Argonne
A G. MADDOCK, Cambridge
L. E J. ROBERTS, Harwell
E J W VERWEY, Eindhoven

EDITORIAL ADVISORY BOARD

U K and Commonwealth J S ANDERSON, F R S, Teddington C C ADDISON, Nottingham C B AMPHLETT, Harwell F M BREWER, Oxford G E COATES, Durham J F DUNCAN, Melbourne H J EMELÉUS, F R S, Cambridge F FAIRBROTHER, Manchester J H GREEN, Kensington, N S W H M N H IRVING, Leeds L E ORGEL, Cambridge A R POWELL, F R S, Wembley P L ROBINSON, Newcastle-upon-Tyne R SPENCE, Harwell H G THODE, F R S, Hamilton L YAFFE, Montreal

U S A L F AUDRIETH and JOHN C BAILAR JR, Univ of Illinois F BASOLO, Northwestern Univ E O BRIMM, Linde Air Products HERBERT C BROWN, Purdue ANTON B BURG, Univ South Calif CHARLES D CORYELL, M I T R W DODSON, Brookhaven W CONARD FERNELIUS, Koppers Company, Penn WARREN C JOHNSON, Chicago H B JONASSEN, Tulane Univ JACOB KLEINBERG, Univ of Kansas K A KRAUS, Oak Ridge W F LIBBY, Los Angeles W M MANNING, Argonne THERALD MOELLER, Univ of Illinois EARL L MUETTERTIES, Wilmington, Delaware EUGENE G ROCHOW, Harvard GLENN T SEABORG, Univ of California P W SELWOOD, Evanston F H SPEDDING, Ames R W STOUGHTON, Oak Ridge J R VAN WAZER, Missouri DON M YOST, Pasadena, Calif W H ZACHARIASEN, Chicago R A PENNEMAN and B B CUNNINGHAM, Univ of California H TAUBE, Chicago

Austria E BRODA, Vienna BERTHA KARLIK, Vienna V GUTMANN, Vienna
Denmark J BJERRUM, Copenhagen
France J BÉNARD, Paris J CHÉDIN, Paris J GUÉRON, Paris M MAGAT, Paris
Germany W HIEBER, Munich G JANDER, Berlin A MUENSTER, Frankfurt
Netherlands A E VAN ARKEL, Leiden A H W ATEN JR, Amsterdam
J H DE BOER, Geleen J H VAN SANTEN, Eindhoven
Israel M BOBTELSKY, Jerusalem *Italy* V CAGLIOTI, Rome
Norway H HARALDSEN, Oslo ODD HASSEL, Oslo
Persia H A C McKAY, Tehran
Sweden G HÄGG, Uppsala L G SILLÉN, Stockholm
Switzerland G SCHWARZENBACH, Zurich

PERGAMON PRESS OXFORD • LONDON • NEW YORK • PARIS

NOTES FOR CONTRIBUTORS

I. General

1 Papers should, in general, be concerned with original work in the field of inorganic and nuclear chemistry They should be submitted to the Editors, whose names and addresses follow (papers not in the English language to Dr E J W Verwey) —

Joseph J Katz *Argonne National Laboratory*, 9700 *South Cass Avenue, Argonne, Illinois, U S A*
A G Maddock *University Chemical Laboratory, Lensfield Road, Cambridge, England*
L E J Roberts *Atomic Energy Research Establishment, Harwell, Didcot, Berks, England*
E J W Verwey *Philips Research Laboratories, Eindhoven, The Netherlands*

2 Fifty free reprints of each paper are supplied Additional copies can be supplied at a reasonable cost if ordered at the time when the first proofs are returned A reprint order form will accompany proofs

II Script Requirements

1 Scripts should be submitted in duplicate They must be typewritten, and double-spaced Authors are requested to make clear any Greek characters which may be confused with ordinary letters or with other characters Authors will receive proofs for correction when their contribution is first set, but there is rarely time for page proofs also to be sent for checking This will be done, however, where the amount of alteration makes it advisable

2 Illustrations should be placed at the end of the manuscript, and legends should be typed on a separate sheet It is requested that photographs should be kept to the minimum necessary Line drawings or good photo-prints may be provided Line drawings must include all relevant details if they are already well drawn it may be possible to reproduce them direct from the original It is not possible to reproduce from "dye-line" prints, or from prints with weak lines Illustrations for reproduction should normally be about twice the final size required Any lettering on diagrams—other than Greek letters, symbols, etc—should be stencilled and should be sufficiently large and bold to permit reproduction when the diagram has been reduced to a size suitable for inclusion in the journal

3 References should be clearly indicated in the text by superior numbers Full references should be given in numbered footnotes containing author's name, initials, title of paper (where desired), abbreviated title of journal, year, volume number, and page number

4 The text of articles submitted must be concise and in a readily understandable style The technical description of the methods used should only be given in detail when such methods are new The essential contents of each paper should be briefly recapitulated in an abstract French and German papers should be submitted with English abstracts **Four copies of the English abstracts are required with all papers, including those in the English language.**

5 To conserve space, authors are requested to mark less important portions of the paper (such as description of methods, record of experimental results, etc) for printing in smaller type

Publishing Offices Headington Hill Hall, Oxford (*Oxford* 64881)

Issued in parts Subscription per annum, including postage (*A*) £33 (*U S A* $100), (*B*) *for subscribers who write direct to the publisher certifying that the subscription is for their personal use,* £5 5s (*U S A* $15) *Back numbers, price on application*

Copyright © 1963 *Pergamon Press Ltd*

PRINTED IN NORTHERN IRELAND AT THE UNIVERSITIES PRESS BELFAST

LIST OF CONTENTS

No 1 March

G W Watt and J W Vaughn Complexes of mercury(II) with palladium(II) chloride and with isobutylene 1
R J Kern Acrylonitrile and propionitrile complexes of metal chlorides in the first transition series 5
Y Sano and H Tanabe Oxygen-carrying Co(II)-histidine complex 11
E R Tucci and N C Li Metal complexation with pyrimidine derivatives II Spectrophotometric studies 17
J C Fanning and H B Jonassen The reaction of 8 quinolinol with copper(II) salts 29
S K Dhar and F Basolo Thermal decomposition of the tris(2 2′-bipyridine) complexes of some first row transition group elements in the solid state 37
R G Charles, A Perrotto and M A Dolan The pyrolysis of divalent metal 8-quinolinol chelates 45
J Shankar, K S Venkateswarlu and C Gopinathan The chemistry of protactinium I The nature of species in HCl solution by solvent extraction and paper electrophoresis 57
M Allbutt and G W A Fowles The reaction of zirconium halides with solutions of potassium and potassium amide in liquid ammonia 67
S M Kulifay A low temperature synthesis for powder form intermetallics and other compounds II Selenides 75
E H Long and J F Sackman Studies on arsenic tetroxide I The interaction of arsenic trioxide and arsenic pentoxide 79
E H Long and J F Sackman Studies on arsenic tetroxide II The combustion of arsenic in oxygen under pressure 87
E H Long and J F Sackman Studies on arsenic tetroxide III Determination of the heat of formation 93
L J Bailin and H B Jonassen Solubilities and effective oxidation states of some lower molybdenum chlorides in concentrated sulphuric acid and related solvents 97
M Shiloh, M Givon and K S Spiegler Ruthenium(VIII) in nitric acid 103
T Sato The extraction of uranium(VI) from nitric acid solutions by di-(2-ethylhexyl)-phosphoric acid 109
D R Gere and C E Meloan Water associated with the bis(8 quinolinol) dioxouranium(VI) chelate extracted into chloroform 117
C M Cook Jr The systems NaCl $CrCl_3$ and KCl $CrCl_3$ 123

Notes

I J Gal and Dj M Petkovic The adsorption of di-n butylphosphate from organic solutions on some metal oxides 129
J R Grove and L Raphael The U V spectrum of aqueous BrCl 130
W E Dasent and T C Waddington The infrared spectrum and structure of I_2O_4 133
E K C Lee and F S Rowland A change in radioactive product distribution for recoil tritium reactions in the solid phase at −196°C 134

Letters to the editors

G Blasse The structures of $ZnLiVO_4$ and $ZnLiNbO_4$ 136
A V Grosse The viscosity of liquid plutonium predicted from a general relationship between the activation energy and melting points of metals and the experimental data 137
Book Reviews 139
Errata 142

No 2 March

H Diamond and J E Gindler Alpha half lives of ^{211}Po ^{217}At and ^{215}Rn 143
F D S Butement and G B Briscoe Neutron-deficient isotopes of yttrium and zirconium 151
C Furlani, E Cervone and V Valenti Electronic structure and spectra of tetrahalogenoferrates(II) 159
K Aida Infra red absorption spectra and structure of biuret hydrogen peroxide complexes 165
C M Harris and E D McKenzie The preparation and colour of tris-2 2′-bipyridyl- and bis 2 2′ 2″ terpyridylrhodium(III) salts 171
A G Massey and N R Thompson Some reactions of tetra(dimethylamino)diboron 175
C E Coffey Synthesis and alkylation of $[Fe(CN)_4(C_2H_5)(CO)]$ $[Mo(CN)_2(C_2H_5)(CO)_3]$ $[W(CN)_2(C_2H_5)(CO)_3]$ and $[W(CN)(C_2H_5)(CO)_4]$ 179
W F Sager, A Fatiadi, P C Parks, D G White and T P Perros The reaction between metallic potassium and carbon monoxide the precursors of the potassium salt of hexahydroxybenzene 187

S N Misra, T N Misra and R C Mehrotra Organic salts of lanthanide elements—I Preparation of triacylates of lanthanum and cerium(III) from aqueous solutions 195
S N Misra, T N Misra and R C Mehrotra Organic salts of lanthanide elements—II Preparation of lanthanum of cerium(III) acylates from a non-aqueous medium 201
L Baroncelli, G Scibona and M Zifferero The effect of additives and stabilizers on the extraction behaviour of U(VI) and Pu(IV) nitrates with tertiary amines 205

Notes

D P Graddon and L Munday Copper(II) cyclopropane-1 amino-1 carboxylate and cyclobutane-1 amino-1 carboxylate 215
S C Srivastava and K Dey The 1 1 beryllium(II) sulpho-dichloro hydroxy-dimethyl fuchson dicarboxylic acid chelate 217
B Keisch Conversion coefficient for the Ir^{191m} transition 220
G J Moody and J D R Thomas Oxidations of the iodide ion in concentrated hydrochloric acid solution 222
S Tsujimura, D Cohen, C L Chernick and B Weinstock The attempted preparation of AmF_6 226

Letters to the editors

T Moeller and S Lanoux Some pentachloro n-alkylamino-triphosphonitriles 229
G Blasse The crystal structure of some compounds of the type $LiMe^{3+}Me^{4+}O_4$ and $LiMe^{2+}Me^{5+}O_4$ 230
L P Harbulak and M J Albinak Preparation of cis-dinitrobis(ethylenediamine) cobalt(III) nitrite 232
A D Kirshenbaum and J A Cahill The direct determination of the normal boiling point of tin 232
W J McDowell and C F Coleman Reagent dependence in sodium and strontium extraction by di(2 ethylhexyl) phosphoric acid 234

No 3 April

A Clearfield and E J Malkiewich Complexes formed by the reaction of zirconium tetrachloride with amides 237
G R Horton and W W Wendlandt The heats of dissociation of the 8-quinolinol and substituted 8-quinolinol metal chelates of uranium(VI), thorium(IV) and scandium(III) 241
G R Horton and W W Wendlandt X-ray and differential thermal analysis studies on the 8-quinolinol and substituted 8-quinolinol metal chelates of thorium(IV), uranium(VI) and scandium(III) 247
C J M Rooymans A phase transformation in the wurtzite and zinc blende lattice under pressure 253
L H Brixner X-ray study and thermoelectric properties of the $NbSi_xGe_2$, and the $TaSi_xGe_2$, systems 257
S C Saxena and E L Taylor Isotope exchange of the oxygen atoms in molecular sieve adsorbents with water and carbon dioxide 261
L Baetslé Ion-exchange properties of zirconyl phosphates III Influence of temperature on tracer ion equilibria 271
W L Marshall and R Slusher Aqueous systems at high temperature—VIII The solubility of UO_3 hydrates in HNO_3-H_2O solutions 25 350 C 10^{-3}-6 molal nitrate 283
D F C Morris and E L Short The extraction lithium chloride by tri-n-butyl phosphate 291

Notes

P C Krueger and M E Kenney Phthalocyaninoruthenium derivatives 303
L Newman On the synergistic effect in solvent extraction 304
J E Earley and J H Gorbitz Mechanism of an oxidation of Cr(II) in the presence of pyrophosphate 306
M Abedini, C H van Dyke and A G MacDiarmid Preparation of disilanyl chloride and disilanyl bromide by the reaction of disilane with hydrogen halide 307
S R Mohanty and S R Upadhyay Annealing of chemical radiation damage in crystalline barium nitrate 309
P Rama Murthy and C C Patel Crystal structure of thorium perchlorate tetrahydrate by X-ray method 310
J R Maurey and E Wolff The partial molal volumes of OCN^- $SeCN^-$ ReO_4^- BF_4^- SO_3F^-, $SO_3NH_2^-$ 312
Y Koda Distillation of ruthenium tetraoxide with volatile acids 314
J Bjerrum Absorption spectra and configuration of the ammine complexes of copper(II) 315
A V Grosse The empirical relationship between the activation of energy viscosity of liquid metals and their melting points 317
D S Popplewell The preparation of ^{210}Bi by a Szilard-Chalmers reaction 318
W Dembinski, A Deptula and B Volavšek Homogenous precipitation and X-ray diffraction studies of urea uranate 320
J Buckley and H G Heal New polymeric sulphur nitrides 321
F M Brewer, J R Chadwick and G Garton The reaction of gallium dichloride with water and hydrogen sulphide 322
F M Brewer, J R Chadwick, G Garton and D M L Goodgame Reactions of HCl and HI with Ga_2Cl_4 324
C C Wang, M Zaheeruddin and L H Spinar Preparation and properties of aluminum phosphide 327
Book Reviews 329

No 4 April

A V Grosse and A D Kirshenbaum The densities of liquid iron and nickel and an estimate of their critical temperature 331
R Schmutzler Phosphorus–fluorine chemistry—I Fluorides of phosphonic and phosphinic acids 335
H Selig and J G Malm The preparation and properties of pertechnetyl fluoride, TcO_3F 349
E R Clark Complex formation between organic thio-acids and germanic acid 353
M S Kachhawaha and A K Bhattacharya Conductometric and spectrophotometric study of the system manganese chloride-salicyloyl hydrazide 361
R D Whealy and R L Yeakey A preparative study of the reaction between antimony(III) bromide and amine hydrobromide compounds 365
M M Jones, A T Davila, J E Hix Jr and R V Dilts Thermodynamics of solution of some inner complex salts II 369
K Madeja und E König Zur Frage der Bindungsverhaltnisse in Komplexverbindungen des Eisen(II) mit 1,10-Phenanthrolin 377
G R Choppin and P J Unrein Halide complexes of the lanthanide elements 387
T D George and W W Wendlandt The thermal decomposition of metal complexes II Some ammine and ethylenediamine complexes of nickel(II) 395
M M Markowitz A basis for the prediction of the thermal decomposition products of metal perchlorates 407
A Liberti, V Chiantella and F Corigliano Mononuclear hydrolysis of titanium(IV) from partition equilibria 415
W B Brown G W Pope, J F Steinbach and W E Wagner Countercurrent extraction of the rare-earth acetylacetonates 429
T Sato The extraction of uranium(VI) from sulphuric acid solutions by tri n-octylamine 441
S Adar R K Sjoblom R F Barnes, P R Fields E K Hulet and H D Wilson Ion-exchange behaviour of the transuranium elements in $LiNO_3$ solutions 447
C G R Nair and A R V Murthy Hydrolytic reactions of tetrasulphur tetranitride in a homogenous medium 453

Notes

M E A Hermans and T Markestein Ammonium uranates and UO_3-hydrates-ammoniates 461
E Hatzopoulos Un nouveau dispositif generateur d Iode 132 462
W J Jenkins Use of sulphamic acid for dissolving plutonium 463

No 5 May

R H Iyer, C K Mathews, N Ravindran K Rengan D V Singh M V Ramaniah and H D Sharma Fission of ^{232}Th by reactor neutrons mass-yield curve 465
P N Dimotakis and M I Stamouli γ-Annealing of nuclear recoil atoms 473
H W Kirby Residue adsorption I Separation of strontium-90 and yttrium 90 483
J A Cahill and A D Kirshenbaum The density of liquid bismuth from its melting point to its normal boiling point and an estimate of its critical constants 501
W R May and M M Jones Adducts of bis(2 4-pentanediono)-copper(II) with pyridine bases stability constants and heats of reaction 507
J L Bear, G R Choppin and J V Quagliano Complexes of the lanthanide elements with mercaptocarboxylate ligands 513
H J Harries Complex formation by n-substituted acetoacetamides I Acid dissociation constants and stability constants of the beryllium complexes 519
M Mercer and R T M Fraser Formation and dissociation of copper(II) nitrosyl complexes in non-aqueous solvents 525
W W Wendlandt and E Sturm The thermal dissociation of potassium methyl- and ethyl-sulphates Thermogravimetric analysis differential thermal analysis gas evolution and X ray studies 535
W W Wendlandt Thermal decomposition of metal complexes III Stoichiometry of the thermal dissociation of some hexamminecobalt(III) complexes 545
E H P Cordfunke and A A van der Giessen Pseudomorphic decomposition of uranium peroxide into UO_3 553
M Schmidt und H Ruf Dimethylgermaniumselenid 557
W L Marshall, R Slusher and E J Smith Aqueous systems at high temperature IX Investigations on the system Li_2SO_4 H_2SO_4 H_2O and its D_2O analogue 200-470 C solubilities and critical phenomena 559
H Galal-Gorchev and W Stumm The reaction of ferric iron with orthophosphate 567
M J Freedman The state of molybdenum(VI) in perchloric acid solutions 575
M Zangen Some aspects of synergism in solvent extraction I Uranium(VI) 581
S E Bryan, M L Good and G J Maus Extraction of group VIII metals by long chain alkyl amines V Liquid ion-exchange behaviour of the cyanide complexes of iron cobalt and nickel 595
I Warshawsky Stability of a dilute solution of sodium in liquid ammonia 601

No 6 June

M J Cabell and L J Slee The ratio of thermal neutron capture to fission for ^{239}Pu 607
E Hagebø The pile neutron fission yields of ^{127}Sb and ^{129}Sb 615
A Halpern Hot atom chemistry of halogens activated in β-decay—II Bond formation between radioiodine and toluene 619
D C Stupegia B Smith and K Hamm Fast neutron capture in ^{232}Th 627

E Lieber, C N R Rao and F M Keane Phenyl lead(IV) azides preparation properties and infra-red spectra 631
M E Frazer, W Gerrard and R Twaits Triphenylphosphine oxide complexes of non-transition metal halides 637
V Y Labaton, S G Donn, R H Watson and J Whitehead Kinetics of the reaction of hydrogen with zirconium titanium alloy 641
H Mabuchi On the volatility of some polonium compounds 657
H Mabuchi Steam distillation of polonium compound with diphenylcarbazide 661
C A Bank and E A Th Verdurmen Oxygen exchange between CO and CO_2 667
C A Bank and E A Th Verdurmen The exchange of oxygen between CO_2 and O_2 677
K Moedritzer and J R van Wazer Studies on phosphorus sulphides 683
Yu A Zolotov and I P Alimarin Investigation of the chemistry of pentavalent neptunium 691
V Vesely and V Pekarek A study of sorption on zirconyl phosphate and changes of its properties at higher temperatures 697
D B James The processing of plutonium by ion exchange I The concentration dependence of distribution coefficients on Dowex 1X4 from 7 M nitric acid 711

Notes

Yu A Zolotov and I P Alimarin The separation of ^{239}Np 719
P Lang and N C Li On the formaton of ternary M(II)-citrate-imidazole complexes 720
K Rengan, M V Ramaniah and N Ravindran Relative yields of ^{111}Pd and ^{111m}Pd in the decay of ^{111}Rh 725
P C Debets X-ray diffraction on hydrated uranium peroxide 727
K S Venkateswarlu and P Charan Das Extraction of thallium(III) from hydrochloric acid solutions 730
E Steger and J Rost Über die von Rice, Daasch, Holden und Kohn(1) beschriebenen Phosphornitrid-Chloridbromide 732
Y Koda Separation of pure ^{90}Y from a ^{90}Sr ^{90}Y mixture by co-precipitation with ferric hydroxide 733
H Ihle, H Michael and A Murrenhoff A spectrophotometric investigation of the synergic solvent extraction system uranyl ion/tri-(n-octyl) phosphine oxide (TOPO)/di(2-ethylhexyl) phosphoric acid (D2EHPA) 734
J D Eakins and D G Humphries Preparation of technetium metal 736
G Franz Synthesis of anhydrous aluminium perchlorates 737
D Dollimore and D Nicholson The thermogravimetric analysis of some complex oxalates 738

Letters to the editors

P del Marmol and P E Fettweis On the decay of ^{72}Zn 741
P H Crayton and W A Thompson Potassium pentachlorovanadium(III) 742
G Blasse The structure of some new mixed oxides containing lithium 743
Book Reviews 745
Erratum 748

No 7 July

J Lerner Half-life of ^{85}Kr 749
J F Facetti Distribution of radioactive antimony formed by neutron capture in antimony compounds 759
R W Ramette and O Anderson On the averred effects of radioisotopic tracers on solubility 763
D S Urch The perbromate problem 771
E L Amma Single crystal data of some tetrameric aluminium alkoxides 779
L H Brixner X ray study and thermoelectric properties of the USi_xGe_{3-x} system 783
S Maričić, P Strohal and Z Veksli Nuclear magnetic resonance studies in the series ZrF_4–xHF–$y$$H_2O$—I The constitution of the hydrates of zirconium tetrafluoride 789
L K Matson, J W Moody and R C Himes Preparation and properties of some uranium selenides and tellurides 795
P A Chopard and R F Hudson Some adducts of phosphines and amines with borane 801
R J Berni, R R Benerito, W M Ayres and H B Jonassen Metal ion complexes of 2-imidazolidinone (ethylene urea) 807
L C Thompson Complexes of the rare earths—V Piperidine-2,6-dicarboxylic acid 819
K Starke Iron(III) dimethoxide compounds 823
J M Andrews, J L Fergusson and C J Wilkins Phosphorus thiobromides 829
W W Wendlandt The thermal decomposition of metal complexes—IV Some amine complexes of copper(II) sulphate 833
W W Wendlandt and J P Smith Thermal decomposition of metal complexes—V Some halopentamminecobalt (III) halide complexes 843
K J Notz and H H Jaffe' Pyrolysis of uranium compounds—I Uranyl sulphate 851
T P Dirkse, L A Vander Lugt and H Schnyders The reaction of silver oxides with potassium hydroxide 859
Y Marcus and I Eliezer The anion exchange of metal complexes—XII The cadmium and mercury–halide systems 867
T Moeller and S G Kokalis The Lewis-base behaviour of some hexa-*n*-alkylamino triphosphonitriles 875
T H Siddall, III Bidentate organophosphorus compounds as extractants—I Extraction of cerium, promethium and americium nitrates 883

Notes

E GIESBRECHT, G VICENTINI and M PERRIER Hafnyl triphosphates 893
M C MEHRA and K KANI Precipitation of tungstates of silver and lead 896
J O SAWYER The polyalkaline earth uranates Sr_2UO_5 and Ca_2UO_5 899
M SPIRO A study of transference and solvation phenomena 903
R L SCHAAF Diosmium oxyoctachloride 904
Erratum 905

No 8 August

S ARONSON Bromine exchange in graphite bromine lamellar compounds 907
I WARSHAWSKY A study of the sodium residue from a dilute solution of sodium in liquid ammonia 919
G R ARGUE and J J BANEWICZ Some properties of the platinum iodides 923
A FINCH and P J GARDNER Association in cyclic boronates and borates 927
H KON Study of the quinquevalent chromium compounds by ESR and optical spectra 933
P C DEBETS and B O LOOPSTRA On the uranates of ammonium—II X-ray investigation of the compounds in the system NH_3–UO_3 H_2O 945
J E MROCHEK, J W O'LAUGHLIN, H SAKURAI and C V BANKS Gem-bis(disubstituted-phosphinyl) alkanes—II Extraction of uranium(VI) with bis(di-*n*-hexylphosphinyl) methane 955
P C H MITCHELL The co-ordination chemistry of molybdenum—I Some complexes of molybdenum(V) with 2 2-dipyridyl 963
S C MALHOTRA Some alkyl isocyanide complexes of iron 971
D F C MORRIS, E L SHORT and D N WATERS Zinc chloride and zinc bromide complexes—III Structures of species in solution 975
W W WENDLANDT and J P SMITH Thermal decomposition of metal complexes—VI Some ammine cobalt(II) complexes 985
D H BROWN Complexes of tetraperoxyditungstate ions with mandelic and glycollic acids 995
F G SHERIF and K I MICHAIL Azide complexes of palladium(II) in solution 999
N MAHADEVAN, R M SATHE and CH VENKATESWARLU Spectrophotometric study of complexes of titanium with sulphosalicylic acid and EDTA using auxiliary complexing agents in the Job's method 1005
Y BASKIN and N S KRISHNA PRASAD Studies of ETA complexes with metal ions—II Investigations of some tetravalent complexes in the solid state 1011
W L MARSHALL and E V JONES Aqueous systems at high temperature—X Investigations on the systems UO_3–CuO–SO_3–D_2O UO_3–NiO–SO_3–D_2O, and UO_3 CuO–NiO–SO_3–D_2O 260 410 C, liquid liquid immiscibility and critical phenomena 1021
W L MARSHALL and J S GILL Aqueous systems at high temperature—XI Effect of pressure on liquid liquid immiscibility in the system UO_2SO_4 H_2O and liquid-supercritical fluid equilibria in the system UO_2SO_4–H_2SO_4–H_2O, 290 430 C, 75 330 bars 1033
L C A THOMPSON and R PACER The solubility of indium hydroxide in acidic and basic media at 25 C 1041
F CERRAI and C TESTA Separation of rare earths by means of small columns of Kel-F supporting di(2-ethylhexyl)orthophosphoric acid 1045
M ZANGEN Some aspects of synergism in solvent extraction—II Some di-, tri- and tetravalent metal ions 1051

Notes

A F CLIFFORD and A K MUKHERJEE Reaction of sodium Π-cyclopentadienyldicarbonylferrate(O) with trimethylsulphonium iodide Trimethylsulphonium salts as methylating agents 1065
J W FRAZER and V L DUVAL The synthesis of 1-nitro-2-(n oxy-n′ fluorodiazine) tetrafluoroethane 1066
D H BROWN, R H NUTTALL and D W A SHARP The thermal decomposition of Ni (pyridine)$_4$ Cl_2 and the preparation of Ni (pyridine) Cl_2 1067
J KRTIL and J ZEMANOVA Exchange properties of ammonium salt of 12-heteropolyacids—VI Sorption of cerium, ruthenium, zirconium and niobium on ammonium phosphotungstate and isolation of ^{137}Cs from an aged mixture of fission products 1069
Errata 1072

No 9 September

M F WEIZEN and K S TOTH Isomeric yield ratios of ^{44}Sc produced by the ^{14}N bombardment of ^{32}S and ^{31}P 1073
W S LYON Decay of ^{131}Ba ^{131}Cs 1079
L PHILLIPS, R C GATTI, R BRANDT and S G THOMPSON Spontaneous fission half lives of ^{254}Cf, ^{256}Fm and ^{246}Cf 1085
R C GATTI R BRANDT, L PHILLIPS and S G THOMPSON Discovery of a new fermium isotope 1089
J B GRUBER On the spectrum of tripositive neptunium in single crystals of lanthanum trichloride 1093
R TUNDER and B SIEGEL The SF_5^- anion 1097
C DJORDJEVIĆ and V KATOVIĆ Co-ordination complexes of niobium and tantalum—I Complex formation of niobium and tantalum pentahalides and niobium(V) oxychloride with acetylacetone in alcohol solutions and formation of oxo-dichloro-acetylacetonato niobium(V) 1099
N A FRIGERIO and R F COLEY Complexes of uranyl ion with dimethylformamide and semicarbazide 1111
F ZADO On molybdenum and tungsten dioxides and dioxydichlorides 1115

A Glasner E Levy and M Steinberg Thermal decomposition of yttrium oxalate in vacuum and in various atmospheres 1119
E Vratny and F Gugliotta The thermal decomposition of lead nitrate 1129
A P Young and C M Schwartz High pressure reactions of CaO and CdO with uranium oxide 1133
R A Horne Kinetics of the iron(II)-iron(III) electron exchange reaction in ice media 1139
T R Bhat and M Krishnamurthy Spectrophotometric studies on protonated ammino and hydroxo complexes of copper(II) nickel(II) and cobalt(II) versenates 1147
C C Patel and G V Jere Nature stability and bonding of the peroxy group in peroxy titanium compounds 1155
W A Baker Jr and F M Gaesser The rate of aquation of *trans*-chlorothioureabis(ethylenediamine)cobalt(III) cation and analogous substituted thiourea complexes 1161
M L Good S E Bryan F F Holland Jr and G J Maus Nature of the hydrogen ion effect on the extraction of Co(II) from aqueous chloride media by substituted ammonium chlorides of high molecular weight 1167
D F Peppard G W Mason and C M Andrejasich Applicability of certain organo phosphorus extractants to environmental and biological radioactive surveys 1175

Notes

J Krtil and E Krivy Exchange properties of ammonium salts of 12-heteropolyacids V Sorption of alkali metals on ammonium phosphomolybdatotungstate 1191
Aneesuddin Malik and S M Fazlur Rahman Spectrophotometric and potentiometric investigations on Mn(III) 1 8 dihydroxy naphthalene 3 6 disulphonic acid chelate 1193
W A Baker Jr and M Daniels Dicyandiamide copper(II) complexes and the metal ion catalysed addition of alcohols to a nitrile 1194
D C Hoffman Half lives of some rare earth nuclides 1196
D A Edwards The preparation and some properties of molybdenum(V) oxotrichloride 1198
Erratum 1200

No 10 October

E Hagebø Relative yields of the pairs ^{97}Nb ^{97m}Nb and ^{98}Nb–^{99}Nb in fission of Pb Bi Th and U induced by 15 157 MeV protons 1201
I F Crowell and H H Willis The yields of the isomers of ^{81}Se and ^{83}Se in the thermal neutron fission of ^{239}Pu 1213
C R McCoy and R L Allred Chemical shifts of the methyl derivatives of the representative elements 1219
J H Grimes A J Huggard and S P Wilford The stabilities of the alkaline earth chelates of some polyaminopolycarboxylic acids 1225
H B Jonassen J O Terry and A D Harris The complex formed between the 5 trifluoromethyl tetrazolyl ion and some transition metal ions 1239
K Saito and M Tsuchimoto A kinetic study of the isotopic exchange of indium between the indium ion and its ethylenediamine-N N N′ N′-tetra acetate in water 1245
J Selbin H R Manning and G Cessac Ligational effects in vanadyl complexes 1253
A Indelli and G Saglietto The reaction between uranyl nitrate and sodium trimetaphosphate 1259
R P Mitra D V S Jain A K Banerjee and K V R Chari Photolysis of sodium nitroprusside and nitroprussic acid 1263
W W Wendlandt and J P Smith The thermal decomposition of metal complexes VII A thermomagnetic study of the Co(III) → Co(II) reduction in cobalt(III) ammine complexes 1267
M F Barrett, D Sweasey and N L Topp The extraction of lanthanons with alkali metal amalgams -III Studies of model systems 1273
J D Corbett R J Clark and T F Munday Solution of metals in their molten salts Some manganese chromium uranium and antimony systems 1287

Notes

G S Rao M S Subramanian and G A Welch Thermal decomposition of plutonium oxalates 1293
E B Brackett T E Brackett and R L Sass The crystal structure of calcium bromide 1295
R B King The formation of mercury derivatives in reactions involving sodium derivatives of metal carbonyls prepared from sodium amalgam 1296
F P Roberts E J Wheelwright and H H van Tuyl Detection of ^{148}Pm among the products of uranium fission 1298

Letter to the editors

A J Walter A method of purification of protactinium from niobium 1301

No 11 November

R W Hoff, F Asaro and I Perlman Alpha decay of neutron-deficient astatine isotopes 1303
J A Panontin and N Sugarman Thick target recoil measurements 1321
M Halmann and L Kugel Thermal neutron capture in gaseous and liquid phosphines II Non volatile products, primary retention and scavenger effects 1343
S Siekierski and R Olszer Relation between the partition coefficient of GeX_4 molecules (X = Cl, Br, I) and the solubility of the solvent 1351
J Selbin, L H Holmes, Jr and S P McGlynn Electronic structure, spectra and magnetic properties of oxycations —IV Ligation effects on the infra-red spectrum of the vanadyl ion 1359

S K K Jatkar, V S Jatkar and A J Mukhedkar Electron polarization and diamagnetic susceptibility 1371
S S Katiyar and V B S Chauhan Stability of iron(III) chelate of cresotic acids a spectrophotometric study of iron(III) m-cresotic acid chelate 1375
K Noack Infra-red spectrum and structure of di-cyclopentadienyl di-iron tetracarbonyl 1383
L Sacconi and A Sabatini The infra-red spectra of metal(II)-hydrazine complexes 1389
C D Schmulbach and C Derderian The synthesis of 1,1-dichloro-3,3,5,5-tetraphenylcyclotriphosphonitrile from a linear phosphonitrile 1395
T Moeller and S G Kokalis The relative rates of reaction of trimeric and tetrameric phosphonitrilic halides with *n*-propylamine 1397
F Koubek and J O Edwards The formation of cobaltic acetate in the catalytic decomposition of peroxyacetic acid 1401
A W Struss and D F Martin The preparation of metal β ketoimine compounds by chelate exchange 1409
A Glasner, F Levy and M Steinberg Thermal decomposition of europium(III) oxalate 1415
J Fuger and B B Cunningham Heats of formation of $Pu_{(aq)}^{3+}$ $PuCl_{3(c)}$ $PuOCl_{(c)}$, $Am^{3+}_{(aq)}$ $AmCl_{3(c)}$ and $AmOCl_{(c)}$ 1423
D L Lewis and R K Murmann Rates of isotopic ligand exchange of Ni(II) complexes of α-amineoximes 1431
J O Wear Rate laws for the U(IV)–U(VI) exchange reaction in aqueous-organic mixed solvent systems 1445
Y Marcus, M Givon and G R Choppin Anion exchange of metal complexes- XIII The actinide(III) nitrate system 1457
I Eliezer and Y Marcus The anion exchange of metal complexes XI Application of the constant ionic medium method to the mercury halide system 1465

Note

M M Chamberlain and A F Greene, Jr Differential thermal analysis of some cyano and cyanonitrosyl iron complexes 1471

No 12 December

B Jezowska-Trzebiatowska and W Wojciechowski The nature of the oxygen-bridge bond in co-ordination compounds 1477
D H Brown and J D McCallum Complexes of tungstate and molybdate ions containing two organic ligands 1483
T H Larkins, Jr and M M Jones The effect of co ordination on the reactivity of aromatic ligands - IX Some reactions of the optically active arsenic (V)-catechol complexes 1487
F D Peat, P J Proll and L H Sutcliffe The effect of temperature on the size of small molecules Applications to some cobalt(II) complexes 1491
W W Wendlandt, W R Robinson and W Y Yang The thermal decomposition of metal complexes –VIII Some diaquotetramminecobalt(III) and haloaquotetramminecobalt(III) halides 1495
C H van Dyke and A G MacDiarmid Formation of diborane by the interaction of disilane with boron trichloride 1503
D R Gere and C E Meloan Water associated with the extraction of tris(4 7-diphenyl-1 10-phenanthroline) iron(II) chelate into chloroform nitrobenzene and 1-decanol 1507
J W Olver and J W Ross, Jr Polarography of zirconium and hafnium in acetonitrile 1515
E A Th Verdurmen and C A Bank Chemical kinetics of oxygen exchange between CO and O_2 1521

Notes

A S Kertes and Y E Habousha On the third phase formation in extraction systems involving aminehydrochlorides 1531
R Levitus and J Raskovan Formation of nitrosyl complexes in the reaction between platinum(II) nitro complexes and concentrated hydrochloric acid 1533
A G MacDiarmid Base catalysed condensation of disilyl sulphide 1534
A M Shams El Din and A A A Gerges Acid base equilibrium constants in fused KNO_3 1537

AUTHOR INDEX

Abedini M 307
Adar S 447
Aida K 165
Albinak M J 232
Alimarin I P 691, 719
Allbutt M 67
Allred A L 1219
Amma E L 779
Anderson O 763
Andrejasich C M 1175
Andrews J M 829
Arcell G R 923
Aronson S 907
Asaro F 1303
Ayres W M 807

Balisel I 271
Bailin L J 99
Baker W A Jr 1161, 1194
Banerjee A K 1263
Banewicz J J 923
Bank C A 667, 677, 1521
Banks C V 955
Barnes R I 447
Baroncelli I 205
Barrett M F 1273
Baskin Y 1011
Basolo F 37
Bear J L 513
Benerito R R 807
Berni R J 807
Bhat T R 1147
Bhattacharya A K 361
Bjerrum J 315
Blasse G 136, 230, 743
Brackett L B 1295
Brackett T F 1295
Brandt R 1085 1089
Brewer F M 322 324
Briscoe G B 151
Brinner L H 257, 783
Brown D H 995 1067, 1483
Brown W B 429
Bryan S E 595 1167
Buckley J 321
Buttement F D S 151

Cabell M J 607
Cahill J A 232, 501
Cessac G 1253
Cerrai E 1045
Cervone F 159
Chadwick J R 322 324
Chamberlain M M 1171
Charan Das P 730
Chari K V R 1263
Charles R G 45
Chauhan V B S 1375
Chernick C L 226
Chiantella V 415
Chopard P A 801
Choppin G R 387, 513, 1457
Clark E R 353
Clark R J 1287
Clearfield A 237
Clifford A F 1065
Coffey C L 179
Cohen D 226
Coleman C F 234
Coley R F 1111
Cook C M Jr 123
Corbett J D 1287
Cordfunke E H P 553
Corigliano F 415
Crayton P H 742
Croall I F 1213
Cunningham B B 1423

Daniels M 1194
Dasent W E 132
Davila A T 369
Debets P C 727, 945
Del Marmol P 741
Dembinski W 320
Deptula A 320
Derderian C 1395
Dey A K 217
Dhar S K 37
Diamond H 143
Diels R V 369
Dimotakis P N 473
Dirkse T P 859
Djordjevic C 1099
Dollimore D 739
Dolan M A 45
Donn S G 641
Duval V I 1066

Eakins J D 737
Earley J E 306
Edwards D A 1198
Edwards J O 1401
Eliezer I 867, 1467

Facetti J J 759
Fanning J C 29
Fatiadi A 187
Fazlur Rahman S M 1193
Fergusson J F 829
Fettweis P I 741
Fields P R 447
Finch A 927
Fowles G W A 67
Franz G 737
Frazer J W 1066
Frazer M J 637
Frazer R I M 525
Freedman M L 575
Frigerio N A 1111
Fuger J 1423
Furlani C 159

Gaesser F M 1161
Gal I J 129
Galal-Gorchev H 567
Gardner P J 927
Garton G R 322, 324
Gatti R C 1085, 1089
George T D 395
Gere D R 117, 1507
Gerges A A A 1537
Gerrard W 637
Giesbrecht E 893
Gill J S 1033
Gindler J E 143
Givon M 103 1457
Glasner A 1119, 1415
Good M L 595, 1167
Goodgame D M L 324
Gopinathan C 57
Gørbitz J H 306, 317
Graddon D P 215
Greene A F Jr 1471
Grimes J H 1225
Grosse A V 137, 321
Grove J R 130
Gruber J 1093
Gugliotta F 1129

Habousha Y I 1531
Hagebø E 615, 1201
Halmann M. 1343
Halpern A 619
Hamm K 627
Harbulak E P 232
Harries H J 519
Harris A D 1539
Harris C M 171
Hatzopoulos T 462
Heal H G 321
Hermans M L A 461
Himes R C 795
Hix J E Jr 369
Hoff R W 1303
Hoffman D C 1196
Holland F F Jr 1167
Holmes L H Jr 1359
Horne R A 1139
Horton G R 241, 247
Hudson R I 801
Huggard A J 1225
Hulet E K 447
Humphries D G 737

Ihle H 734
Indelli A 1259
Iyer R H 465

Jaffe' H H 851
Jain D V S 1263
James D B 711
Jatkar S K K 1371
Jatkar V S 1371
Jenkins W J 463
Jere G V 1155
Jezowska-Trzebiatowski B 1477
Jonassen H B 29, 99, 807, 1239
Jones F V 1021
Jones M M 369, 507 1487

Kachhawaha M S 361
Kant K 896
Katiyar S S 1375
Katović V 1099
Keane F M 631
Keisch B 220
Kenney M E 303
Kern R J 5
Keries A S 1531
King R B 1296
Kirby H W 483
Kirshenbaum A D 232, 321, 501
Koda Y 314, 733
Kokalis S G 875, 1397
Kon H 933
Konig E 377
Koubek L 1401
Krishna Murthy M 1147
Krishna Prasad N S 1011
Krtil J 1069 1191
Krívy I 1191
Krueger P C 303
Kugel L 1343
Kulifay S M 75

Labaton V Y 641
Lanoux S 229
Larkins T H Jr 1487
Lee E K C 133
Lerner J 749
Levitus R 1533
Levy I 1119, 1415
Lewis D I 1431
Li N C 17, 720
Liberti A 415
Lieber F 631
Long L H 79, 87, 93
Loopstra B O 945
Lyon W S 1079

Mabuchi H 657, 661
MacDiarmid A G 307, 1503, 1534
Madeja K 377
Mahadevan N 1005
Malhotra S C 971
Malik A 1193
Malkiewich L J 237
Malm J G 349
Manning H R 1253
Marcus Y 867 1457 1465
Marić S 789
Markishin I 461
Markowitz M M 407
Marshall W L 283, 559, 1021 1033
Martin D I 1409
Mason G W 1175
Massey A G 175
Matthews C K 465
Matson I K 795
Maurey J R 312
Maus G J 595 1167
May W R 507
McCallum J D 1683
McCoy C R 1219
McDowell W J 234
McGlynn S P 1359
McKenzie E D 171
Mehra M C 896
Mehrotra R C 195, 201
Meloan C L 117, 1507
Mercer M 525
Michael H 734
Michail K F 999
Misra S N 195, 201
Misra T N 195, 201
Mitchell P C H 963
Mitra R P 1263
Moedritzer K 683
Moeller T 229, 875, 1397
Mohanty S R 309
Moody G J 221
Moody J W 795
Morris D F C 291, 975
Mrochek J E 955
Mukhedkar A J 1371
Mukherjee A K 1065
Munday L 215
Munday I F 1287
Murmann R K 1431
Murrenhoff A 734
Murthy A R V 453

Nair C G R 453
Newman L 304
Nicholson D 739
Noack K 1383
Notz K J 851
Nuttall R H 1067

O Laughlin J W 955
Olszer R 1351
Olver J W 1515

Pacer R 1041
Panontin J A 1321
Parks P C 187
Patel C C 310, 1155
Peat F D 1491
Pekárek V 697
Peppard D F 1175
Perlman I 1303
Perrier M 893
Perros T P 187
Perrotto A 45
Petković Dj M 129
Phillips L 1085, 1089
Pope G W 429
Popplewell D S 318
Proll P J 1491

Quagliano J V 513

Rama Murthy P 310
Ramaniah M V 465 725
Ramette R W 763
Rao C N R 631
Rao G S 1293
Raphael I 130
Raskovan J 1533
Ravindran N 465, 725
Rengan K 465 725
Roberts I P 1298
Robinson W R 1495
Rooymans C J M 253
Ross J W Jr 1515
Rost J 732
Rowland F S 133
Ruf H 557

Sabatini A 1389
Sacconi L 1389
Sackman J F 79 87, 93
Sager W F 187
Saglietto G 1259
Saito K 1245
Sakurai H 955
Sano Y 11
Sass R L 1295
Sathe R M 1005
Sato I 109, 441
Sawyer J O 899
Saxena S C 261
Schaap R L 903
Schnyders H 859
Schmidt M 557
Schmulbach C D 1395
Schmutzler R 335
Schwartz C M 1133
Scibona G 205
Scrivastava S C 217
Selbin J 1253, 1359
Selig H 349
Shams El Din A M 1537
Shankar J 57
Sharma H D 465
Sharp D W A 1067
Sherif F G 999
Shiloh M 103
Short E L 291, 975
Siddall T H III 883
Siegel B 1097
Siekierski S 1351
Singh D V 465
Sjoblom R K 447
Slee L J 607
Slusher R 283, 559
Smith B 627
Smith F J 559
Smith J P 843, 985 1267
Spiegler K S 103
Spinar L H 326
Spiro M 902
Stamouli M I 473
Starke K 823
Steger I 732
Steinbach J F 429
Steinberg M 1119 1415
Strohal P 789
Struss A W 1409
Stumm W 567
Stupegia D C 627
Sturm I 535
Subramanian M S 1293
Sugarman N 1321
Sutcliffe L H 1491

Tanabe H 11
Tang P 720
Taylor T I 261
Terry I O 1239
Testa C 1045
Thomas J D R 221
Thomeson I C 819
Thompson I C A 1041
Thompson N R 175
Thompson S G 1085 1089
Thompson W A 742
Topp N I 1273
Toth K S 1073
Tsuchimoto M 1245
Tsujimura S 226
Tucci I R 17
Tunder R 1097
Twaits R 637

Unrein P J 387
Upadhyay S R 309
Urch D S 771

Valenti V 159
van der Giessen A A 553
Vander Lugt L A 859
van Dyke C H 307 1503
van Tuyl H H 1298
van Wazer J R 683
Vaughn J W 1
Veksli Z 789
Venkateswarlu Ch 1005
Venkateswarlu K S 57, 730
Verdurmen E A Th 667 677 1521
Vesely V 697
Vicentini G 893
Volavsek B 320
Vratny F 1129

Waddington T C 132
Wagner W F 429
Walter A J 1301
Wang C C 326
Warshawsky I 601 919
Waters D N 975
Watson R H 641
Watt G W 1
Wear J O 1445
Weinstock B 226
Welch G A 1293
Wendlandt W W 241, 247, 395, 535, 545 833 843, 985, 1267 1495
Wetzen M L 1073
Whealy R D 365
Wheelwright F J 1298
White D G 187
Whitehead E 641
Wilford S P 1225
Wilkins C J 829
Willis H H 1213
Wilson H D 447
Wojciechowski W 1477
Wolff J 312

Yang W Y 1495
Yeakley R L 365
Young A P 1133

Zado F 1115
Zaheeruddin M 326
Zangen M 581, 1051
Zemanová J 1069
Zifferero M 205
Zolotov Yu A 691, 719

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 1 to 3. Pergamon Press Ltd. Printed in Northern Ireland

COMPLEXES OF MERCURY(II) WITH PALLADIUM(II) CHLORIDE AND WITH ISOBUTYLENE

G. W. Watt and J. W. Vaughn*
Department of Chemistry, University of Texas, Austin, Texas

(*Received* 9 *April* 1962)

Abstract—The principal insoluble solid product of the reaction between isobutylene and mercury(II) sulphate in 10 per cent sulphuric acid is mercury(I) sulphate; a yellow mercury–olefin complex that could not be isolated is also formed. The interaction of Hg^{2+} and Pd^{2+} in the presence of chloride ion results in a 1:1 complex which is interpreted as a bridged species involving chloride ion and water ligands.

It has been observed(1) that when isobutylene was added to 1.0 M $HgSO_4$ and 0.23 M $PdCl_2$ in 10% H_2SO_4 at 0°, a bright yellow solid of unknown composition separated. We have investigated this reaction as well as the interaction of $HgSO_4$ and $PdCl_2$ in the absence of isobutylene; the results are reported below.

EXPERIMENTAL

Materials and methods

All materials used were reagent grade chemicals. Stock solutions of the salts at the concentrations indicated below were prepared by dissolving appropriate quantities of each in 100 ml of 10% H_2SO_4. For absorption spectra, 5 ml aliquots of, for example, the standard $PdCl_2$ solution was placed in each of seven 25 ml volumetric flasks, different volumes of the stock $HgCl_2$ solution were added to six of these flasks and these solutions were diluted to volume with 10% H_2SO_4, as was the seventh flask that contained only $PdCl_2$. Other solutions were prepared similarly. Spectra in the visible region were obtained using a Beckman Model DU quartz spectrophotometer with matched 1.0 cm silica cells. Optical densities were measured at the absorption maximum of $PdCl_2$ in 10% H_2SO_4 (416–418 mμ); addition of $HgSO_4$ shifted this maximum to significantly shorter wavelengths. Infra-red spectra were studied with KBr pelleted samples and a Baird Model 4-55 infra-red recording spectrophotometer.

Preliminary experiments

Addition of isobutylene to 0.02 M $PdCl_2$ in 10% H_2SO_4 at 0° produced elemental Pd as the only insoluble product; it was identified by X-ray diffraction patterns. Similarly, when the olefin was added to the acid solution containing $PdCl_2$ and $HgSO_4$ (both 0.02 M), the insoluble products consisted of Pd and a bright yellow solid; the latter was shown by analysis to be Pd-free.

The reaction between isobutylene and mercury(II) sulphate

A 1 M solution of $HgSO_4$ in 10% H_2SO_4 was cooled to 0°, filtered and again cooled to 0°. Isobutylene was passed slowly into the solution; after about 5 min a finely divided yellow precipitate began to form. Addition of C_4H_8 was continued for 0.5 hr, then the reaction mixture was allowed to warm to room temperature and was filtered. The yellow solid was washed with two 5 ml portions of 95 per cent ethanol followed by three 5 ml portions of diethyl ether and dried at 70°. Mercury was determined by the tetraiodomercurate method(2) and isobutylene by measuring the volume of gas liberated upon thermal decomposition of the yellow solid initially at 130°, followed by heating to a final temperature of 200 , that the evolved gas consisted of isobutylene was confirmed by gas chromatography (Found Hg, 75 2, SO_4^{2-}, 18 8, C_4H_8, 2 8%) X-ray diffraction data for this product are given in Table 1

---

* Robert A. Welch Foundation Postdoctoral Fellow, 1959–61; present address: Department of Chemistry, Northern Illinois University, DeKalb, Illinois.

(1) W. F. Gresham, Private communication (1960).

(2) G. W. Watt, D. M. Sowards and R. E. McCarley, *Analyt. Chem.* **28**, 556 (1956).

The infra-red spectrum of the yellow solid showed bands at 6 3 (C=C stretch) and 7 7 μ (CH_3 vibration), the corresponding reported frequencies are 5 4-7 4 and 7 3-7 4 μ, respectively

The reaction between mercury (II) sulphate and palladium (II) chloride

As a means of investigating the nature of possible soluble complexes, spectrophotometric data were obtained for solutions containing Hg^{2+} and Pd^{2+} in the presence of the following negative ions Cl^- and SO_4^{2-} SO_4^{2-} only, and Cl and ClO_4 The resulting data are given in Table 2

TABLE 1 —X-RAY DIFFRACTION DATA*

Reaction product		Hg_2SO†	
d(A)	I/I_0	*d*(A)	I/I_0
6 4	0 5	6 4	0 05
5 9	0 5		
5 3	1 0	5 3	0 05
4 6	0 3	4 4	0 8
4 1	0 3	4 2	0 8
3 7	0 2	3 6	0 5
3 5	0 1	3 5	0 5
		3 3	0 1
3 1	0 2	3 2	0 1
2 9	0 1	3 0	1 0
		2 7	0 1
2 6	0 1	2 6	0 5
		2 5	0 1
		2 4	0 5
2 2	0 1	2 2	0 5
2 0	0 1	2 1	0 5

* CuK_α radiation, Ni filter, 40 kV tube voltage, 15 mA filament current, exposure time 10-12 hr, relative intensities estimated visually

† This work

DISCUSSION

The foregoing data show that the principal insoluble solid product of the reaction of isobutylene with $HgSO_4$-$PdCl_2$- 10% H_2SO_4 solution is Hg_2SO_4, the yellow solid could not be separated and purified but is assumed to be a mixture of $Hg(C_4H_8)SO_4$ and Hg_2SO_4 The X-ray data in Table 1 establish the presence of Hg_2SO_4 but do not preclude the presence of $HgSO_4$ and/or HgO If relative intensities are ignored, all but one *d*-spacing (5 9 Å) are attributable to Hg_2SO_4 However, even though relative intensities were only estimated, the data show noteworthy discrepancies in intensities (particularly among the most intense lines) and this suggests an unusual frequency of coincidences

If only Hg_2SO_4 and $Hg(C_4H_8)SO_4$ are present in the insoluble product, a one gram sample would contain 3 74 10^{-3} mole Hg and 4 83 × 10^{-4} mole $Hg(C_4H_8)SO_4$ When the analytical data are corrected for the presence of the latter, the resulting Hg^+/SO_4^{2-} ratio is 2 2 1

Since olefin oxidation would be expected to yield products having high vapour pressure, these are assumed to have been removed during the washing and drying operations. Thus, retention of hydrocarbon should be restricted to bonded olefin, this conclusion is compatible with the data given above The infra-red spectrum shows retention of the carbon–carbon double bond in the yellow complex, as was found by CHATT(3) for olefin complexes of platinum.

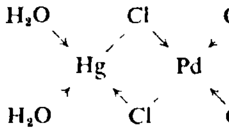
The present results are similar to related cases studies previously CHATT(4) has reported that olefins and $HgSO_4$ react *in acidic solutions to form complex solids of unknown composition* HOFMAN *and* SAND(5) *found that 1-butene reacted with* $HgSO_4$ *in nearly neutral solution to form a bright yellow solid of undetermined constitution* They converted this product to a chloride and expressed the composition as $C_4H_6Hg_4Cl_4O_6$ H_2O plus 7 4 per cent Hg_2Cl_2

With regard to the interaction of Hg^{2+} and Pd^{2+} in solution, a plot of the data in Table 2(A) as optical density vs Hg^{2+}/Pd^{2+} shows a sharp inflexion at a mole ratio of 1 1 1 The same is true for the data of Table 2(C), but those of 2(B) do not show evidence of interaction in the presence of sulphate ion only These results show clearly that chloride ion is involved in the complex and that sulphate ion is not Hence it seems reasonable to assume co-ordination number four for both Hg^2 and Pd^2 in a bridged complex of the type

TABLE 2 —SPECTROPHOTOMETRIC DATA

	Mole ratio Hg^{2+}/Pd^{2+}	Optical density
(A) $HgSO_4$-$PdCl_2$-10% H_2SO_4*	0 00	0 490
	0 33	0 420
	0 50	0 380
	0 83	0 308
	1 67	0 250
	2 50	0 255
	3 33	0 264
(B) $HgSO_4$-$PdSO_4$-10% H_2SO_4†	0 00	0 220
	1 00	0 215
	2 00	0 216
	3 00	0 219
	4 00	0 218
(C) $HgClO_4$-$PdCl_2$-10% $HClO_4$‡	0 00	0 490
	0 83	0 237
	1 67	0 153
	2 50	0 150
	3 33	0 156

* Wave length, 416 mμ, stock solutions ca 0 01 M
† Wave length, 418 mμ, stock solutions ca 0 005 M
‡ Wave length, 414 mμ, stock solutions ca 0 01 M



but the data presently available to not permit a choice between chloride ions or water molecules (or both) as the bridging ligands Attempts to isolate this complex by paper chromatography and ion exchange techniques were unsuccessful

Acknowledgements—This work was supported by the Robert A Welch Foundation and the U S Atomic Energy Commission

---

(3) J CHATT, *J Chem Soc* 2939 (1953)
(4) J CHATT, *Chem Revs* **48,** 14 (1951)
(5) K A HOFMAN and J SAND, *Ber Chem Dtsch Ges* **33,** 1353 (1900)

J Inorg Nucl Chem, 1963, Vol 25, pp 5 to 9 Pergamon Press Ltd Printed in Northern Ireland

ACRYLONITRILE AND PROPIONITRILE COMPLEXES OF METAL CHLORIDES IN THE FIRST TRANSITION SERIES

R J. KERN
Monsanto Chemical Company, St Louis 66, Missouri

(*Received* 8 *May* 1962)

Abstract—*Acrylonitrile and propionitrile complexes of metal chlorides in the transition series from titanium to zinc were isolated and characterized The two nitriles differ in their patterns of reaction with* $CrCl_3$, $FeCl_3$ *and* $NiCl_2$

RECENT advances in polymerization catalysis have made available new stereoregular forms of many terminal olefins and other vinyl monomers. However, attempts to polymerize acrylonitrile, a monomer of considerable economic importance, in stereospecific fashion have not as yet been successful As part of an approach to developing a catalyst system for this task, the acrylonitrile and propionitrile complexes of metal chlorides in the first transition series were prepared Some aspects of their synthesis and chemistry are also of interest in the field of co-ordination complexes

Information on the composition and appearance of these materials is presented in Table 1. The only practical solvent for most of them is the bulk parent nitrile itself Other solvents, which are usually polar in nature, themselves tend to displace the nitrile from the co-ordination sphere As exceptions, the complexes of $TiCl_4$, $TiCl_3$, $FeCl_3$ and $ZnCl_2$ are soluble in benzene with the last two somewhat soluble in chloroform Presumably nitriles containing more carbon atoms would exhibit increased solubility in hydrocarbons

Most complexes (Table 1) were in solution at some stage during synthesis But, as unique cases, those formed from $MnCl_2$ were not The nitrile ligands were assimilated directly on the $MnCl_2$ lattice without solution occurring as an intermediate step

Acrylonitrile, but not propionitrile, requires the presence of zinc metal as a catalyst to form a complex with $CrCl_3$ The zinc may be recovered without discernible change (see also Reference 1)

Air oxidation of the VCl_3 3AN complex in the presence of benzene gave rise to the vanadyl derivative The product is believed to be a clathrate with benzene Well-formed blue crystals obtained from several preparations all analysed the same, $VOCl_2(AN)_2\,(C_6H_6)_{0\,42}$ A green complex VCl_3 2AN has been reported from the reaction of VCl_4 and acrylonitrile (2)

Exactly one-third of the iron (moles) in the crystalline complex derived from $FeCl_3$ and acrylonitrile appears in the ferrous state This reduction is accompanied by the chlorination of acrylonitrile Why reduction should proceed to just this extent is not clear Perhaps a crystal lattice packing effect is responsible If one postulates iron with co-ordination numbers of four and six, then the empirical formulas for acrylonitrile and propionitrile ferric chloride complexes are compatible with the formulations

---

(1) W HERWIG and H ZEISS, *J Org Chem* **23**, 1404 (1958)
(2) L K CASE, *U S Pat* 2930807 (1960)

TABLE 1 —ACRYLONITRILE (AN) AND PROPIONITRILE (PN) COMPLEXES

Empirical formula	Colour	Physical form	Metal (%) Calc	Metal (%) Found	Cl (%) Calc	Cl (%) Found	Remarks*
$TiCl_3$ 3AN	Green	Sandy	15 3	15 2	34 0	33 9	
$TiCl_3$ 3PN	Royal blue	Crystals	15 0	15 0	33 4	33 4	$Xg = 2\ 70 \quad 10^{-6}$, $\mu = 1\ 59$
$TiCl_4$ 2AN	Yellow	Waxy	16 2	16 1	47 9	47 7	m p 128–9 dec
$TiCl_4$ 2PN	Yellow	Waxy	16 0	16 0	47 3	47 1	m p 105–6°
VCl_3 3AN	Purplish-black	Cubes	16 1	16 0	33 5	33 4	
VCl_3 3PN	Purplish-black	Cubes	15 8	15 6	33 0	32 6	
$VOCl_2(AN)_2\ (C_6H_6)_{0\ 42}$	Royal blue	Crystals	18 7	18 4	25 6	25 5	Clathrate ?
$CrCl_3$ 3AN	Purplish-black	Cubes	16 4	16 3	33 5	33 4	$Xg = 19\ 4 \times 10^{-6}$, $\mu = 3\ 87$
$CrCl_3$ 3PN	Purplish-black	Cubes	16 1	16 1	32 9	32 9	$Xg = 16\ 1 \quad 10^{-6}$, $\mu = 3\ 85$
$MnCl_2$ AN	White	Pulp	30 6	30 9	39 6	39 6	$Xg = 85\ 1 \times 10^{-6}$, $\mu = 6\ 02$
$MnCl_2$ PN	White	Pulp	28 6	28 9	37 0	37 0	
$FeCl_2$ AN	Tan	Sandy	31 1	31 4	39 4	39 0	
$FeCl_2(FeCl_3)_2(AN)_6$	Golden	Crystals	21 8	21 6	36 8	36 8	$Xg = 56\ 2 \times 10^{-6}$, $\mu = 5\ 86$
$(FeCl_3)_3(PN)_5$	Red brown	Crystals	22 0	21 8	41 8	41 7	
$CoCl_2$ AN	Blue	Crystals	32 2	32 2	38 8	38 7	$Xg = 61\ 5 \quad 10^{-6}$, $\mu = 5\ 16$
$CoCl_2$ PN	Blue	Crystals	31 9	32 5	38 4	38 8	
$NiCl(AN)_{2\ 2}$	Brownish-orange	Powder	27 8	27 7	16 8	16 5	$Xg = 1\ 76 \times 10^{-6}$, $\mu = 1\ 04$
$NiCl_2(AN)_3$	Royal blue	Crystals	20 4	20 5	24 5	24 3	
$NiCl_2(AN)_{1\ 1}$	Pale yellow	Powder	31 1	30 9	37 8	37 7	
$NiCl_2$ 2PN	Royal blue	Cubes	24 5	24 2	29 6	29 2	$Xg = 5\ 47 \times 10^{-6}$, $\mu = 1\ 82$
$NiCl_2(CH_3CN)_{3\ 5}$	Royal blue	Crystals	21 5	21 6	26 0	26 1	Acetonitrile
$CuCl_2(AN)_{0\ 5}$	Orange-brown	Powder	39 5	39 5	44 0	43 8	$Xg = 9\ 03 \times 10^{-6}$, $\mu = 1\ 87$
$CuCl_2(PN)_{0\ 4}$	Tan	Powder	40 7	40 4	45 4	45 5	$Xg = 9\ 26 \times 10^{-6}$, $\mu = 1\ 90$
$ZnCl_2$ 2AN	White	Crystals	26 9	27 7	29 3	29 6	m p 38–40°, very hygroscopic

* Xg = gm magnetic susceptibility, cgs units, μ = permanent magnetic dipole moment, Bohr magnetons

$FeCl_2(AN)_4$ $2FeCl_3(AN)$ and $FeCl_3(PN)_3{\cdot}2FeCl_3PN$ The former tends to crystallize much more readily than the latter

Nickel chloride complexes. Anhydrous $NiCl_2$ is insoluble in and unreactive toward these nitriles However, nickel chloride complexes will form in the presence of metallic zinc. In contrast to its purely catalytic role for $CrCl_3$ complex formation, zinc is here a reactant also reducing the bulk of $NiCl_2$ to nickel metal

Propionitrile and acetonitrile give rise to well formed blue crystals of nickel chloride complexes in yields under 25 per cent Under the same conditions acrylonitrile extracts a brown colour from the $NiCl_2/Zn$ mixture After extraction has proceeded for some time an orange–brown powder which contains nickel and chlorine in equimolar amounts appears in the pot. This powder, analysing as $NiCl(AN)_{2\ 2}$, is quite insoluble in acrylonitrile. In fact, the material is so insoluble that it must have formed from the soluble brown material extracted from the $NiCl_2$–Zn mixture after passing through the paper extraction thimble On treatment with 1M HCl this orange–brown powder gives rise to small amounts of polyacrylonitrile

The striking difference between acrylonitrile and the saturated nitriles in their reactions with $NiCl_2$ suggests participation of the vinyl group in the former. The infra-red spectrum of the orange-brown product reveals that the vinyl group has disappeared Further, the nitrile stretch is a doublet shifted to lower frequencies (2225 and 2199 cm^{-1}) in contrast to the usual shift of this band to higher frequencies on complexing (see Table 2) A dimeric pi-complexed allyl nickel bromide $(C_3H_5NiBr)_2$ has been reported recently (3)

A blue crystalline complex of $NiCl_2$ and acrylonitrile with vinyl groups intact was prepared by a different route Acetonitrile in the nickel chloride–acetonitrile complex was displaced by acrylonitrile and the complex crystallized from acrylonitrile solvent

Infra-red spectra The propionitrile complexes revealed little change from the spectrum of propionitrile itself The —C≡N stretching band shifts 30–50 cm^{-1} to higher frequencies in the complexes This is true of the acrylonitrile complexes also (see Table 2) and it has previously been observed on other nitrile complexes (4,5)

More striking is the splitting of the 970 cm^{-1} non-planar vinyl proton band of acrylonitrile This splitting was evident in all AN complexes (except the orange $NiCl_2$ derivative discussed above) but was most pronounced for those members of the series $MnCl_2$ through $CuCl_2$ (see Table 2)

Vinyl CH and CH_2 out-of-plane deformation vibration frequencies which appear at 980 and 910 cm^{-1} in normal olefins occur as a single, strong, broadened band at 970 cm^{-1} in acrylonitrile (6) The splitting of this 970 cm^{-1} band when acrylonitrile complexes probably indicates improved differentiation of the two vinyl C—H vibration frequencies

EXPERIMENTAL

General Anhydrous materials were employed throughout Operations were conducted under oil-pumped prepurified Airco nitrogen Usually the powdered metal chloride (and zinc dust if required as stated in the text) was extracted with bulk liquid nitrile in a Soxhlet apparatus Caking of the metal halide in the thimble may be alleviated by admixture of dry sand The soluble chlorides ($TiCl_4$, $TiCl_3$, VCl_4, $FeCl_3$ and $ZnCl_2$) may be dissolved directly in hot bulk nitrile The corresponding

---

(3) F O FISCHER and G BURGER, *Z Naturforsch* **16 B**, 77 (1961)

(4) H J COERVER and C CURRAN, *J Amer Chem Soc* **80**, 3522 (1958)

(5) G S RAO, *Z Anorg Chem* **304**, 351 (1960)

(6) H W THOMPSON and P TORKINGTON, *J Chem Soc* 599 (1944)

TABLE 2.—ABSORPTION FREQUENCIES IN COMPLEXES OF ACRYLONITRILE

Complex of	$C\equiv N$ Stretch	Non-planar vinyl proton bending	
None	2232 cm^{-1}	970 cm^{-1}	
VCl$_3$	2275	986	968
CrCl$_3$	2280	997	970
MnCl$_2$	2267	975	962
FeCl$_2$	2263	974	957
FeCl$_3$	2265	981	957
Co$_2$Cl	2265	972	959
NiCl$_2$	2290	978	963
NiCl	2225, 2199		
CuCl$_2$	2290	978	960
ZnCl$_2$	2248, 2280	985	960

complex crystallizes out on standing. Manganese dichloride must be covered directly with the nitrile because its insolubility precludes extraction.

NiCl$_2$–Acetonitrile and NiCl$_2$–Propionitrile. Powdered anhydrous yellow NiCl$_2$ (5 g), 5 g dry washed white sand and 0.5 g zinc dust were ground in a dry mortar in a nitrogen dry-box. This mixture was extracted with refluxing nitrile. A blue colour concentrated in the pot from which royal blue crystals developed on standing overnight. These were isolated under nitrogen, rinsed with dry benzene and dried in a stream of dry nitrogen. The nitrile complex of ZnCl$_2$ also produced is much more soluble than the nickel chloride complex both in nitrile and in benzene.

Orange-brown nickel chloride–acrylonitrile complex. The procedure above for NiCl$_2$–acetonitrile was carried out except that acrylonitrile was substituted for acetonitrile. A brownish-orange powder precipitated from the liquors after a few hours which was isolated, washed with benzene and dried. This air-stable material was insoluble in water, ethanol, benzene and dimethylformamide.

The product was boiled about 10 min in 1M aqueous HCl whereon it became flocculant and a brighter orange in colour while the aqueous liquors became green. The filtered orange solids gave rise to a viscous solution in dimethylformamide. After centrifuging, the viscous supernatant liquors were poured into methanol. A grayish flocculant solid precipitated which behaved like known polyacrylonitrile on compression molding.

NiCl$_2$–Acrylonitrile. Crystals of NiCl$_2$–acetonitrile complex (2 g) prepared as above were placed in a baked nitrogen-purged 50 ml flask. Twenty millilitres of freshly distilled acrylonitrile was added. The solvent liquors were carefully evaporated from the resulting solution under mechanical pump vacuum through a nitrogen manifold. Fresh AN (20 ml) was again added and the process repeated for a total of four times. The final solution was allowed to stand two days. A pale yellow powder precipitated which was filtered under dry nitrogen, rinsed with benzene and dried. Its infra-red spectrum clearly revealed complexed acrylonitrile with a split 970 cm^{-1} vinyl proton band (see Tables 1 and 2).

After three more days, blue crystals developed from the above filtrate. They were isolated by decantation, rinsed with dry benzene and dried in a nitrogen stream. The infra-red spectrum was very similar to that of the yellow powder above revealing a strong split 970 cm^{-1} vinyl proton band.

FeCl$_3$–Acrylonitrile. Black anhydrous FeCl$_3$ (20 g) was extracted from a Soxhlet thimble with an 80 ml charge of acrylonitrile. Large greenish-yellow crystals developed from the extraction liquors. They were soluble in water and in chloroform. Iron content was determined by dissolving the crystals in water, boiling off the liberated AN, reducing with SnCl$_2$ and titrating with K$_2$Cr$_2$O$_7$.(7) Ferrous iron was determined in a similar manner except liberated AN was distilled off under nitrogen and no SnCl$_2$ treatment was employed.

Oxidation of VCl$_3$(AN)$_3$. Eight grammes of VCl$_3$(AN)$_3$ were dissolved in 100 ml acrylonitrile, then 50 ml of wet benzene was added. Air was slowly bubbled through this solution for 24 hr at about 25°. Hexane was added until a slight turbidity developed which just disappeared on swirling. The solution was then filtered and set aside at 0° whereon blue crystals developed. Sometimes crystal formation is difficult to obtain at this point. Use of seeds helps. Or a gentle application of reduced pressure, without agitation, often gives rise to crystal formation at the vessel-wall solution-surface juncture as evaporation occurs. Alternatively, the oxidized acrylonitrile-benzene solution may be filtered and the hexane carefully introduced to form a supernatant layer. Crystallization is often prone to occur at the interface Yield, 0 2–1 g of blue crystals strongly resembling hydrated copper sulphate On drying *in vacuo*, a deeper shade of blue develops

---

(7) H. H. WILLARD and N. H. FURMAN, *Elementary Quantitative Analysis*, p. 248. Van Nostrand, New York (1942).

A weighed quantity of these dried crystals were placed in a volume calibrated 5 mm tube sealed at one end The bare minimum of water necessary to dissolve the crystals was added by hypodermic syringe and needle, whereon, an organic liquid separated from the vanadyl blue aqueous phase The volume of the organic phase was accurately measured Gas chromatography revealed this organic phase to be a mixture of benzene and acrylonitrile present in a mole ratio 0 42 1 The observed volume of this phase checked closely that calculated if one mole unit of AN and 0 42 mole units of benzene were released per mole of crystals based on the empirical formula $VOCl_2(AN)_2\,(C_6H_6)_{0\,42}$ By analogy with $VOCl_2(THF)_3$,(8) it was postulated two molecules of AN per V atom probably existed in the complex and that the benzene was trapped, possibly in a clathrate structure V and Cl analyses corroborated the proposed formula (see Table 1) Analyses were duplicated on two independent syntheses

$ZnCl_2$–*Acrylonitrile* About 20 g of ground $ZnCl_2$ were covered with 100 ml acrylonitrile Heat evolved as a clear colourless solution formed Colourless crystals of the AN complex develop preferably in one direction forming long slivers and rods These crystals are soft and hygroscopic melting at 38–40° When heated to 50–60°/2 mm, the isolated nitrogen-dried crystals melt, then bubble markedly as AN is released After such bubbling ceases, a turbid viscous mass remains This material is soluble in water except for about 1 wt % of insoluble polyacrylonitrile The latter may be compression molded to a film and forms a viscous solution in dimethylformamide

Infra-red spectra Infra-red spectra were obtained from mineral oil mulls on sodium chloride plates using a Beckman IR-IV spectrophotometer

---

(8) R J KERN, *J Nucl Inorg Chem* **24**, 1105 (1962)

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 11 to 15. Pergamon Press Ltd. Printed in Northern Ireland

OXYGEN-CARRYING CO(II)–HISTIDINE COMPLEX

Y. SANO and H. TANABE
Research Laboratories, Takeda Chemical Industries, Ltd., Osaka, Japan

(*Received* 30 *March* 1962, *in revised form* 11 *June* 1962)

Abstract—The oxygen-carrying Co(II) histidine complex has been isolated, and it has been concluded mainly from the infra-red spectra that the complex has no oxygen atoms of oxonium type but a peroxide bridge between two six-co-ordinated cobalt ions. Some properties of the complex are described.

BURK *et al.*[1] found in 1946 that the histidine complex of Co(II) combines reversively with molecular oxygen in aqueous solution. Since then the physicochemical properties of the oxygen-carrying complex in aqueous solution have been fully investigated by some workers,[2] especially by HEARON, and the following facts have been ascertained.

1. Two molecules of bis-histidinato cobalt(II) (A) (pink) combine with one molecule of oxygen, but (A) does not combine with carbon monoxide.
2. The oxygen-carrying complex (B) (brown) changes slowly to the red cobalt(III) complex (C).
3. The only absorption maxima of (A), (B) and (C) in the visible are at 486 mμ (ϵ = 18.4), 385 mμ (ϵ = 1,620) and 490 mμ (ϵ = 125) respectively.
4. (A) has three unpaired electrons, but (B) has none.
5. (A) shows anomalous rotatory dispersion, but the optical rotation of (B) cannot be measured owing to its strong absorption intensity.

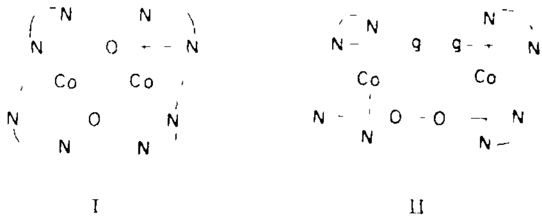


FIG. 1.—Two structures for (B) proposed by HEARON. (g may be water or carboxyl.)

Crystallization of the complex, however, has not been successful, though attempts seem to have been made.[3] Also, no other Co(II) complexes that combine reversibly with molecular oxygen in aqueous solution have been isolated in crystal form. It was reported that the oxygen-carrying Co(II)–glycylglycine complex had been isolated,[4] but later it proved to be a Co(III)–glycylglycine complex having one OH group.[5]

For the structure of (B) HEARON[2] suggested two formulas (I, II) (Fig. 1), and he favoured I since (A) does not combine with carbon monoxide Martell and Calvin, however, preferred a structure analogous to II in their book (6)

---

[1] D. BURK, J. Z. HEARON, L. CAROLINE and A. L. SHADE, *J. Biol. Chem.* **165**, 723 (1946).

[2] L. MICHAELIS, *Arch. Biochem.* **14**, 17 (1947); D. BURK, J. Z. HEARON, H. LEVY and A. L. SCHADE, *Federation Proc.* **6**, 242 (1947); J. Z. HEARON, *Federation Proc.* **6**, 259, 260 (1947); J. Z. HEARON, *J. Natl. Cancer Inst.* **9**, 1 (1948); J. Z. HEARON, D. BURK and A. L. SCHADE, *Ibid.* **9**, 337 (1949).

[3] J. Z. HEARON, *J. Natl. Cancer Inst.* **9**, 7 (1948).

[4] J. B. GILBERT, M. C. OTEY and V. E. PRICE, *J. Biol. Chem.* **190**, 377 (1951); C. TANFORD, D. C. KIRK, Jr. and M. K. CHANTOONI, Jr., *J. Amer. Chem. Soc.* **76**, 5325 (1954).

[5] V. CAGLIOTI, P. SILVESTRONI and C. FURLANI, *J. Inorg. Nucl. Chem.* **13**, 95 (1960).

We have found that brown needle crystals can be obtained by adding alcohol or acetone to a solution of (A) filled with oxygen gas and cooling the mixture. The brown needles were confirmed to be crystals of the oxygen-carrying complex (B) from the facts that under this condition (A), if any, remains in solution, and that an aqueous solution of the crystals shows an absorption maximum at 385 mμ, which disappears when nitrogen gas is filled in the solution But values of the elementary analysis of the crystals did not agree with the calculated values Investigation of the cause of the disagreement revealed that Co(II) in (A) is oxidized fast when the pH value of the solution is high and therefore, Co(III) complex contaminated the crystals Accordingly, almost pure crystals were obtained from the solution of about pH 7, and the value of its elementary analysis agreed with the formula $[Co(C_6H_8N_3O_2)_2]_2O_2$ $3H_2O$

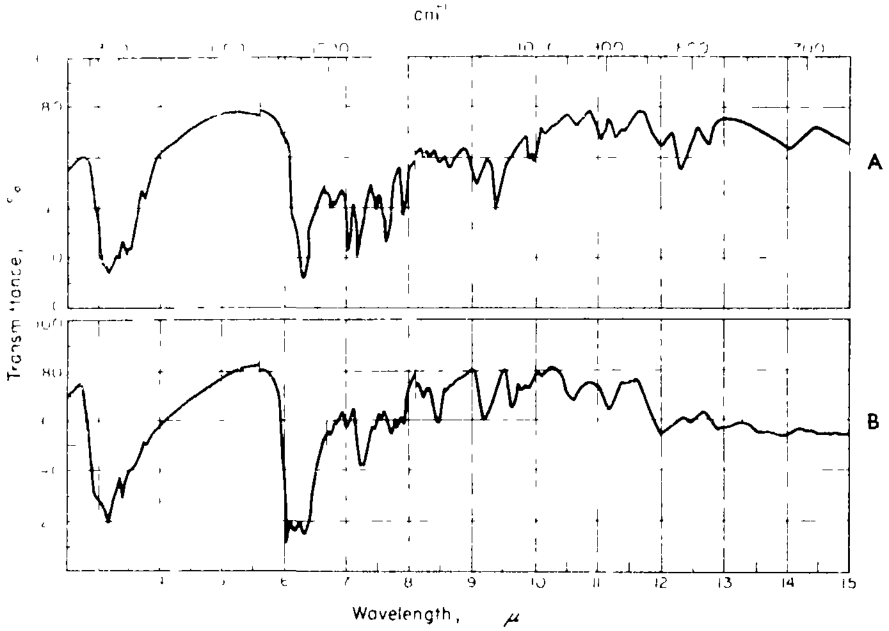


Fig 2 —Infra-red spectra (Nujol and hexachlorobutadiene mull method)
(A) Bis-histidinato cobalt(II) (B) The oxygen-carrying complex

The molecular structure of (B), especially the configuration of the oxygen molecule, was deduced from the infra-red spectra When the infra-red spectra of (A) and (B) (Fig 2) are compared, the difference in the region between 1500 cm^{-1} and 1700 cm^{-1} attracts attention particularly The band at 1582 cm^{-1} in (A) is attributed to the antisymmetric COO stretching vibration, suggesting essentially electrostatic COO-Co bonds The band seems to overlap the scissoring vibration of the amino group In the spectra of bis-histidinato zinc the latter (1621 cm^{-1}) is distinct from the former (1605 cm^{-1}) On the other hand, the spectrum of (B) has three peaks (1656, 1618, 1571 cm^{-1}) in this region The band at 1656 cm^{-1} is assigned, judging from the wave number, to the antisymmetric stretching vibration of the carboxyl group bonded covalently to Co(II). Some examples like this have been reported by Busch *et al* (7) in the spectra of carboxyl groups of EDTA complexes and hydroxyethylethylenediaminetriacetic acid complexes The latter two bands (1618, 1571 cm^{-1}) may be assigned to the antisymmetric stretching vibration of the carboxyl ion and the scissoring vibration of the amino group respectively In (B) the band of the symmetric COO stretching vibration splits slightly into two branches As mentioned above, it seems evident that two kinds of carboxyl groups exist in (B), and this fact was further ascertained from the spectra in heavy water (Fig 3) In the spectra the scissoring vibration of amino group shifts to longer wavelength as a result of deuteration and does not overlap the antisymmetric COO stretching vibration, and there is no possibility that any bands based on the same origin may differ only owing to difference in crystal form The spectrum of (A) has a band attributed to the antisymmetric COO stretching vibration On the other hand, there are two bands assigned to the antisymmetric COO stretching vibration in (B) The presence of two kinds of carboxyl groups indicates that an oxygen molecule in (B) combines with cobalt ions in a peroxide bridge type

---

(6) A E Martell and M Calvin, *Chemistry of the Metal Chelate Compounds*, p 356 Prentice-Hall, New York (1952)

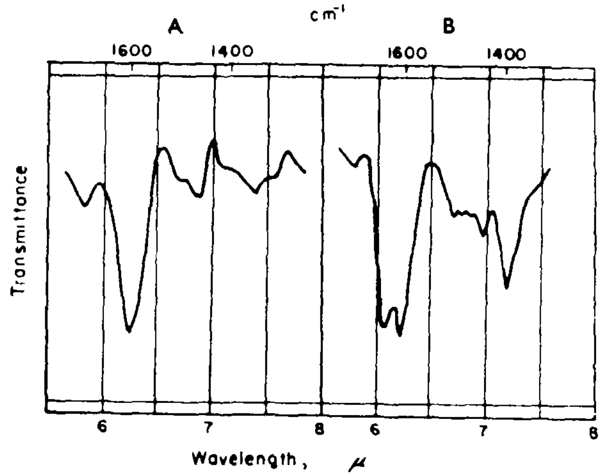


Fig 3 —Infra-red spectra in heavy water
(A) Bis-histidinato cobalt(II) (B) The oxygen-carrying complex

To the complex (A) Hearon assigned a tetrahedral structure from the magnetic moment, but Leberman and Rabin(8) deduced from potentiometric data that histidine is co-ordinated as a tridentate ligand in complexes with cobalt(II), nickel(II) and zinc(II) Recently Earnshaw and Larkworthy,(9) repeating the magnetic measurement, obtained a value, 5 16 B M in solution at 297 2°K, which is consistent with an octahedral structure Since the visible absorption spectrum also supports an octahedral structure as they discussed, it is most probable that the complex (A) takes an octahedral one But the figure in their paper is incorrect, because the ligands in the figure consist of L-histidine and D-histidine After all, there are three probable structures for (A) according to the relative spatial arrangements of ligands in the molecule, one of which is shown in Fig 4 For the structure of (B) the formula in Fig 5 is derived from the structure of (A) Naturally, two alternative structures of (B) may be derived from other structures of (A)

---

(7) D H Busch and J C. Bailar, Jr *J Amer Chem Soc* **75**, 4574 (1953), M L Morris and D H Busch, *Ibid* **78**, 5178 (1956)

(8) R Leberman and B R Rabin, *Trans Faraday Soc* **55**, 1660 (1959)

(9) A Earnshaw and L F Larkworthy, *Nature Lond* **192**, 1068 (1961)

X-ray diffraction patterns of (A) and (B) are shown in Fig 6 As shown in the figure, the pattern of (B) just after being collected on a funnel differs from that after drying

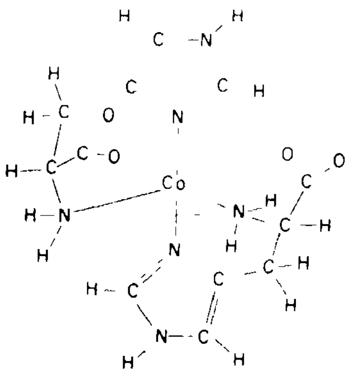


Fig 4 —A probable structure of (A)

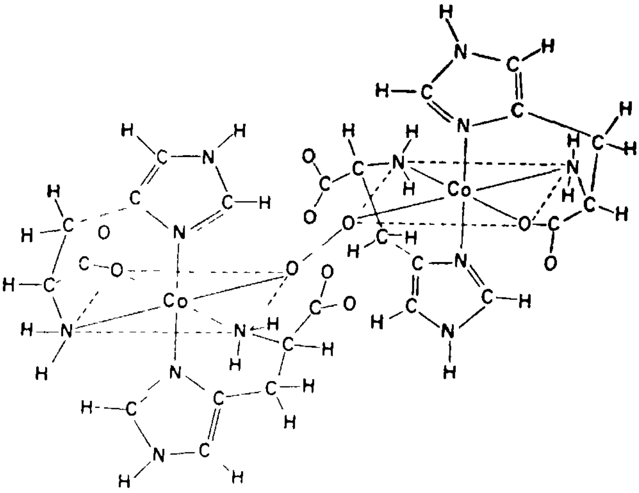


Fig 5 A probable structure of (B)

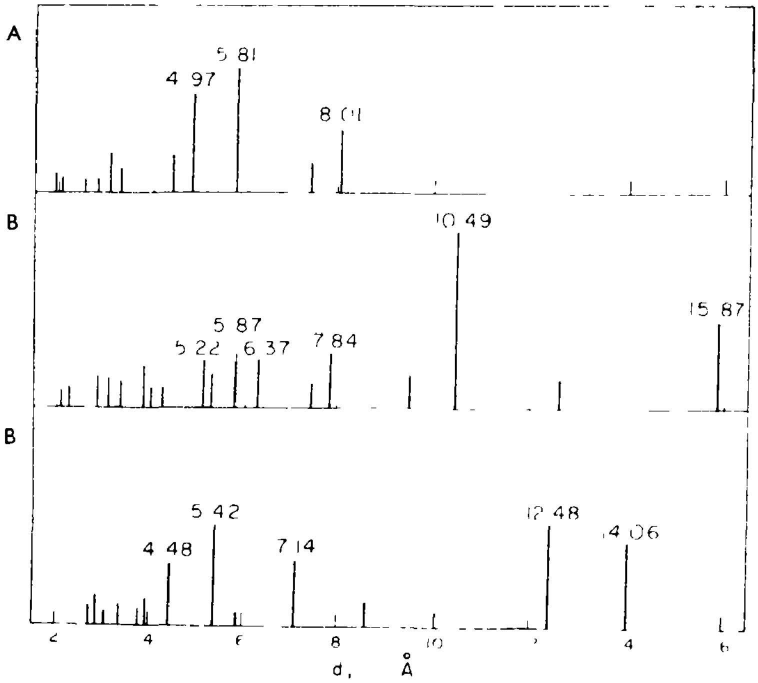


Fig 6 X-ray diffraction patterns (Powder method)
(A) Bis-histidinato cobalt (II) (B) The oxygen-carrying complex just after collecting on a funnel (B') The oxygen-carrying complex after drying

(B) is considerably hygroscopic at room temperature When measured with a heat balance, it begins to lose in weight from 65°C, and the loss in weight is over the loss by crystal water when heated up to 120°C By qualitative investigation oxygen gas was not detected at all, but ammonia gas was detected above 95°C and carbon dioxide above 100°C. Since (A) and bis-histidinato zinc do not decompose at such low temperature, this phenomenon seems to be caused by the bound oxygen molecule

EXPERIMENTAL

Bis-histidinato cobalt (II) (*A*) To a solution containing cobalt (II) suphate 7-hydrate (1 41 g, 5 mmole) and L-histidine (1 55 g, 10 mmole), in which nitrogen gas had been filled previously, 10 ml of 1N NaOH and then 2 5 times its volume of ethanol were added, and the mixture was cooled After the sodium sulphate separated was filtered off, the filtrate was concentrated under reduced pressure in a nitrogen atmosphere until crystallization started The product obtained was a pale pink crystalline powder, 1 0 g (Found Total Co, 15 59, Co (III), 0 08, C, 37 98, H, 4 88, N, 21 78, O, 20 75 Calcd for $Co(C_6H_8N_3O_2)_2H_2O$ Co, 15 30, C, 37 41, H, 4 71, N, 21 82, O, 20 77%)

Oxygen-carrying bis-histidinato cobalt (II) (*B*) To a solution of L-histidine 1-hydrochloride 1-hydrate (1 05 g, 5 mmole) and cobalt (II) chloride 6-hydrate (0 6 g, 2 5 mmole) in 20 ml of water, 9 7 ml of 1N NaOH were added in a nitrogen atmosphere After oxygen gas was passed for about 2 min and 40 ml of acetone were added, the solution was cooled The resulting needle crystals were collected on a funnel, washed successively with 60 per cent acetone, anhydrous acetone and ether, and dried over calcium chloride under reduced pressure to give brown fine needles, 0 6 g (Found Co, 14 30, C, 35 02, H, 4 76, N, 20 07 Calcd for $[Co(C_6H_8N_3O_2)_2]_2O_2\ 3H_2O$ Co, 14 37, C, 35 13, H, 4 67, N, 20 49%)

Bis-histidinato zinc The same procedure as in the synthesis of (A) was employed, using zinc sulphate 7-hydrate and L-histidine White crystals (Found Zn, 15 93 C, 34 88, H, 4 72, N, 20 76 Calcd for $Zn(C_6H_8N_3O_2)\ 2H_2O$ Zn, 15 96, C, 35 18, H, 4 92, N, 20 51%)

Infra-red spectra Spectra were measured with a Perkin-Elmer Model 221 instrument, using a sodium chloride prism Spectra in heavy water were obtained in the following way (A) was dissolved in a ratio of 5 per cent in heavy water filled previously with nitrogen gas, the solution was quickly put in a demountable cell 0 025 mm thick, and the transmittance scale of the photometer was expanded 2 2 times The spectrum of (B) in heavy water was obtained from a solution of (A), into which oxygen gas had been passed The background was corrected by the spectrum of heavy water

X-ray diffraction patterns The X-ray diffraction patterns were obtained with an Isodeflex Model 2 Diffraction Unit, using iron *K*α radiation

J. Inorg. Nucl. Chem. 1963. Vol. 25, pp. 17 to 27. Pergamon Press Ltd. Printed in Northern Ireland

METAL COMPLEXATION WITH PYRIMIDINE DERIVATIVES—II

SPECTROPHOTOMETRIC STUDIES[*]

EDMOND R. TUCCI[†] and NORMAN C. LI
Department of Chemistry, Duquesne University

Abstract—Ultra-violet light absorption studies were made on a number of pyrimidine derivatives in water or deuterium oxide both as a function of pH and in the absence or presence of metal ions. The pyrimidine compounds studied included uracil-5-carboxylic acid (iso-orotic acid), 2-ethylthio-iso-orotic acid, uracil-6-carboxylic acid (orotic acid), 5-nitro-orotic acid and their corresponding esters.

Iso-orotic acid was found to be very pH sensitive in water and deuterium oxide. Identical spectral curves were obtained in both solvent systems. A lowering of the extinction coefficient at pH 6 as compared with pH 1, could indicate an ionization effect rather than enolization since no appreciable wavelength shift was observed. However, enolization is predominant in the region of pH 12. A confirmation that pK_2 in iso-orotic acid refers to proton dissociation from an enolic species was obtained by determining the pK_2 of iso-orotic acid in water and in deuterium oxide. In the presence of Cu(II) ions at pH 3, there was noted a slight shift towards the visible in the region of the uracil absorption band of iso-orotic acid. This slight shift is attributed to complexing through the ketonic oxygen and carboxyl group.

Very little shift in the uracil lactam band occurred in going from the acidic to neutral region for orotic acid and a slight shift to longer wavelengths resulted when approaching the region of pH 12. Ultra-violet absorption spectra obtained in deuterium oxide indicated that even up to pH 12 orotic acid was still predominantly mono or diketonic. Deuterium isotope studies indicate at least one monoketonic form at pH 10. Spectral curves show that in the presence of Zn(II), Co(II) and Mn(II), orotic acid forms weak complexes. However, in the presence of Cu(II) and Ni(II) ions strong complexing is observed. A deuterium isotope effect was noted with orotic acid and Ni(II) ions in deuterium oxide resulting from the cleavage of the D—N_1 bond and verifying complexation through the carboxyl group and nitrogen in the 1-position.

The nitro group in 5-nitro-orotic acid appears to considerably modify the lactam–lactim equilibria in the pyrimidine nucleus, favouring enolization in the neutral and high pH regions. It was found that 5-nitro-orotic acid complexes strongly with Cu(II) at pH 6, but is almost independent of Ni(II) ions.

The ethylthio group in 2-ethylthio-iso-orotic acid appears to cause enhanced enolization of the carbonyl group in the 4-position. Complexing with Cu(II) ions is quite similar to iso-orotic acid in magnitude.

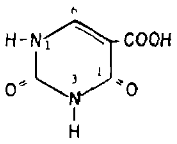
PYRIMIDINE derivatives constitute a very important class of compounds because they are components of the biologically important nucleic acids and have been shown to exert a pronounced physiological effect. Since most living systems contain metal ions which are essential for proper functioning, the question arises as to the effect of such metal ions on nucleic acids. To simplify the problem even further one might consider the effect of metal ions on components of nucleic acids, such as the pyrimidines. Any elucidation of metal-ion effects on the pyrimidine nucleus could possibly lead to a better understanding of complex biological processes occurring in living systems. As part of a general program on metal complexation studies involving biologically important compounds, our work was directed towards an understanding as to the nature of metal binding in pyrimidine acids and their corresponding esters.

---

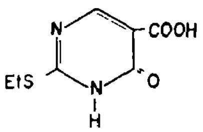
[*] Abstracted from the Ph.D. thesis of E. R. Tucci at Duquesne University and supported by National Science Foundation Grant NSF G-21532.

[†] Presently located at Gulf Research and Development Co., Petrochemical Division, P.O. Drawer 2038, Pittsburgh 30, Pa.

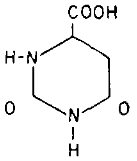
In an attempt to elucidate the complexing sites of a chelating agent, the structural nature of the ligand under the conditions of complexation must first be determined In a consideration of the uracil nucleus the situation presents a rather perplexing problem The complexity of the pyrimidine system results from the effect of pH changes and group substitution on the lactam-lactim (ketonic-enolic) isomerism Previous workers(1 7) have reported preferred structures for the pyrimidine derivatives both in the solid state and in an aqueous medium at various pH values, using spectrophotometric methods This paper presents the results of ultra-violet light absorption studies in a water or deuterium oxide medium in the absence or presence of metal ions, for the following pyrimidine acid derivatives and their corresponding esters uracil-5-carboxylic acid (iso-orotic acid), 2-ethylthio-iso-orotic acid, uracil-6-carboxylic acid (orotic acid) and 5-nitro-orotic acid For the pyrimidine acids, pK_a values were determined by potentiometric methods The pK'_1 value refers to proton dissociation from the carboxyl group and the pK_2 value refers to proton dissociation from the lactam or lactim form Written as the diketonic form, these acids have the following structures



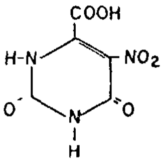
ISOÖROTIC
$pK_1 = 4\ 16$
$pK_2 = 8\ 89$



2-ETHYLTHIO-ISOÖROTIC
$pK_1 = 6\ 01$
$pK_2 = 10\ 52$



OROTIC
$pK_1 = 2\ 07$
$pK_2 = 9\ 45$



5-NITROÖROTIC
$pK_1 = < 1\ 5$
$pK_2 = 4\ 94$

A previous paper(8) reported the potentiometric results on dissociation constants and complex formation constants of several pyrimidine derivatives The results presented in this paper using ultra-violet spectrophotometry appear to support our previous conclusions using potentiometric methods The observed trend in complex stability

---

(1) J Lacher D Campion and J Park, *Science* **110,** 300 (1949)
(2) J Marshall and J Walker, *J Chem Soc* 1004 (1951)
(3) L Short and H Thompson, *J Chem Soc* 168 (1952)
(4) D Brown amd I Short, *J Chem Soc* 331 (1953)
(5) J Loofbourow M Stimson and M Hart, *J Amer Chem Soc* **65,** 148 (1943)
(6) E Blout and M Fields, *J Amer Chem Soc* **72,** 479 (1950)
(7) P Levene, L Bass and H Simms, *J Biol Chem* **70,** 229 (1926)
(8) E R Tucci, F Doody and N C Li, *J Phys Chem* **65,** 1570 (1961).

of the pyrimidine derivatives in our ultra-violet light absorption studies is in agreement with the results obtained using precision potentiometry and ion-exchange radiochemical methods Complexing sites postulated by potentiometric methods were verified by ultra-violet absorption studies To further substantiate the previous results in a water medium, the ultra-violet spectrophotometric studies were also performed in a deuterium oxide medium It was believed that the structural nature of certain pyrimidine compounds was such as to exhibit a deuterium isotope effect and that this isotope effect would result in a noticeable shift in the wavelength maximum or minimum as a function of pH or metal ion type Results are reported which indicate the existence of a deuterium isotope effect at various pH values and also in the presence of certain metal ions

EXPERIMENTAL

Materials The pyrimidine derivatives, gift of Sigma Chemical Co , St Louis Mo , were dried *in vacuo* at room temperature over calcium chloride Refrigerated stock solutions of these compounds, which were always freshly prepared, were analysed by a determination of their neutralization equivalents using potentiometric methods All chemicals were of C P grade The deuterium oxide (99 8 per cent) was obtained from Bio-Rad Laboratories

Apparatus and procedure A Beckman Model DU quartz spectrophotometer equipped with a photomultiplier attachment as well as a Cary Model 14 Automatic Recording Spectrophotometer, were employed for spectrophotometric measurements

In the ultra-violet light absorption studies, standard solutions of the pyrimidine derivatives were diluted to 10^{-4} or 10^{-5} molar concentration Each solution was adjusted to the desired pH by use of a Beckman Model G pH Meter The concentration of metal solutions used in spectrophotometric studies of metal complexing depended on the desired metal-ligand ratio, but was generally 10^{-4} mole/l The pH region was selected such that maximum complexing occurred when the metal ligand ratio was 1 1 or 10 1 and there was no interference due to metal hydrolysis

RESULTS AND DISCUSSION

In studying the ultra-violet light absorption spectra of the pyrimidine derivatives the method of MARSHALL and WALKER[(7)] was employed The pK_a values of all the substances being examined by ultra-violet spectral methods were first determined by potentiometric titrations The ultra-violet spectra were then measured in aqueous solution at pH values approximately two units from the pK_a values This is to assure that only one species is present in solution

(A) *Iso-orotic acid spectra*

Since ultra-violet light absorption studies considered in this paper are concerned with monocarboxylic acid pyrimidine derivatives, it is essential to consider the effect of the carboxyl group on the parent uracil structure For iso-orotic acid, the 218 mμ band indicated in Fig 1 agrees with the wavelength values found by other workers[(9)] who have attributed this band to the carboxyl group In the pH range 1–6 there is observed little change in the maxima values of 272-268 mμ, which are attributed to the uracil absorption bands in the keto form However, there is a distinct shift towards the visible of about 23 mμ for the uracil band when one goes from pH 6 to 12 There is also a noticeable shift in the uracil band to longer wavelengths, in the region of pH 12, for uracil itself This shift to longer wavelengths for both iso-orotic acid and uracil at pH 12 is probably the result of further enolization The absorption band for iso-orotic acid is lower at pH 6 than pH 1 This could possibly indicate that at pH 6 the

[(9)] M STIMSON and M REUTER, *J Amer Chem Soc* **65,** 151 (1943) concentration of the keto form diminishes However, since there is observed no enol shift the lowering of the extinction coefficient may result from a change in the extent of ionization of the carboxyl group At pH 12 0 enolization is occurring and therefore

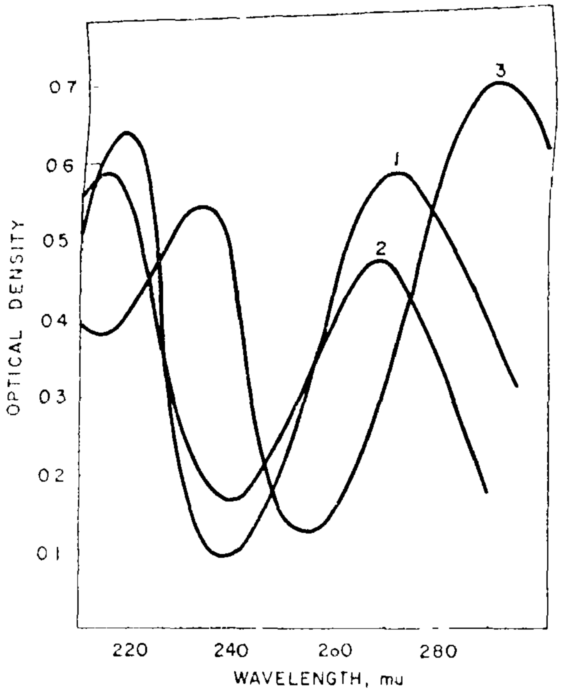
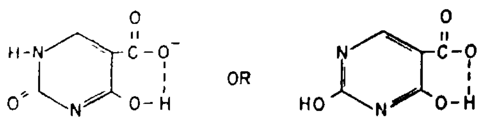


FIG 1 - Ultra-violet absorption spectra of iso-orotic acid in water Curve 1, pH 1 0, 2, pH 6 0, 3, pH 12 0

one observes a wavelength shift The following structures illustrate how stabilization by hydrogen-bonding would favour enol formation for iso-orotic acid in the region of pK_2

HYDROGEN-BOND STABILIZATION OF LACTIM FORM IN ISOOROTIC ACID (pK_2 REGION)



A study was made on the effect of ionization and enolization of iso-orotic acid in deuterium oxide Solutions of iso-orotic acid were prepared using similar conditions as in the water medium and ultra-violet absorption spectra determined An examination of the results indicated no shift in the wavelength maxima or minima so that those values are identical to the water system A confirmation that pK_2 in iso-orotic acid refers to proton dissociation from an enolic species was obtained by determining the pK_2 of iso-orotic acid in water and in deuterium oxide Li *et al* (10) have shown that the deuterium isotope effect, as measured by $pK_{D_2O} - pK_{H_2O}$, is a linear function of pK_{H_2O} for acid dissociation from specific groups and have given equations for calculating $pK_{D_2O} - pK_{H_2O}$ for proton dissociation from various groups. For proton dissociation from the hydroxyl groups in certain compounds containing three polar groups, the following equation may be written

---

(10) N C Li, P Tang and R Mathur, *J Phys Chem* **65**, 1074 (1961)

$$pK_{D_2O} - pK_{H_2O} = 0.132 + 0.072\, pK_{H_2O} \qquad (1)$$

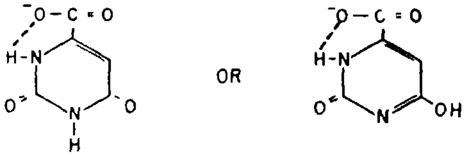
Since pK'_2 *for iso-orotic acid in water is 8.89, the value of* $pK_D - pK_H$ *calculated by* equation (1) is 0.77. The pK_2 value determined for iso-orotic acid in deuterium oxide was found to be 9.72, so that the observed value of $pK'_{D_2O} - pK'_{H_2O}$ is 0.83. The observed isotope effect is in close agreement with the value calculated for proton dissociation from the hydroxyl group and therefore favours the enol structure of iso-orotic acid in the region of pK_2.

Although potentiometric titrations of iso-orotic acid containing metal ions indicated complex formation, it was desirable to see if spectrophotometric methods would be more informative. Iso-orotic acid solutions were prepared containing metal ions which were known to strongly chelate, such as Cu(II) ions. The pH of the solution was adjusted to result in maximum complexing of the metal, as determined by potentiometric methods. It was found that complexing of the Cu(II) ions resulted in only a slight shift towards the visible in the region of the uracil band. From the previous discussion of iso-orotic acid at pH 6.0, the predominant species of the ligand in this experiment is the ketonic form. The carboxyl group was found to be essential for metal complexing iso-orotic acid, since the corresponding ester of iso-orotic acid resulted in no noticeable complexing. Since a change was observed in the absorption, attributed to the ketonic structure when metal ion was added, complexing most probably occurs through the ketonic oxygen and the carboxyl group.

(B) *Orotic acid spectra*

The ultra-violet light absorption spectra were determined for orotic acid in a water or deuterium oxide medium at various pH values. The effect of moving the carboxyl group from the 5-position to the 6-position results in some noticeable differences in the ultra-violet absorption spectrum. In determining the change of light absorption as a function of pH, spectral curves were determined at selected pH ranges to obtain the desired molecular species. These absorption curves in a water medium are illustrated in Fig. 2. There is a shift in the uracil band to higher wavelengths for orotic as compared to iso-orotic acid. However for orotic acid there is very little shift in the uracil keto band in going from the acidic to the neutral region as with uracil itself. Unlike iso-orotic acid and uracil, there is not a large shift to longer wavelengths as one enters the pH 12.0 region for orotic acid. The uracil band at pH 12 was found to be somewhat weakened in orotic acid when the extinction coefficient was compared with iso-orotic acid. This occurrence may perhaps be attributed to an ionization effect of the carboxyl group in the 6-position of the pyrimidine nucleus. The extinction coefficient is not lowered at pH 6.0 for orotic acid as it was in the case of iso-orotic acid. Stimson and Reuter[9] found that there was a decrease in the extinction coefficient as the endpoint for enolization was approached. Although this would appear to offer an explanation for the difference in the extinction coefficients for orotic and iso-orotic acid in the pH 6 region, it is felt that the observed effect is largely due to the difference in the degree of ionization of the carboxyl group. This is further substantiated by the fact that there results a decrease in the extinction coefficient for orotic acid in the region of pH 12 even though no enol shift is indicated. Up to pH 12 therefore, orotic acid is still predominantly in the monoketonic or diketonic form. This was indicated when the ultra-violet absorption spectra were obtained in deuterium oxide. The ultra-violet absorption spectral data on orotic acid and iso-orotic acid indicates that in the pH region above 7·0 iso-orotic acid enolizes much more readily than orotic acid. A confirmation that pK_2 in orotic acid refers to proton dissociation from a ketonic species was obtained by determining the pK_2 of orotic acid in water and deuterium oxide and using Equation (1) to obtain the calculated ΔpK_2. The observed value of $pK_D - pK_H$ was found to be 0·26 as compared with the value of 0·81, calculated from Equation (1). The pK_2 of orotic acid cannot refer to proton dissociation from a hydroxyl group, as was found for iso-orotic acid, but rather from a —NH—CO— structure. The following structures illustrate how stabilization by hydrogen-bonding would favour keto formation for orotic acid in the region of pK_2.

HYDROGEN-BOND STABILIZATION OF
LACTAM FORM IN OROTIC ACID
(pK_2 REGION)



Ultra-violet light absorption studies in water were also performed on metal complexes of orotic acid. Since potentiometric methods showed orotic acid to form weak complexes with zinc, cobalt, manganese and cadmium but strong complexes with copper and nickel, it was desirable to see if this trend could be verified using spectrophotometric methods. Thus, solutions of divalent zinc, cobalt, manganese, copper and nickel containing orotic acid and adjusted to the pH for maximum complexing, were subjected to ultra-violet absorption studies. The absorption curves are shown in Figs 3 and 4. As indicated, only slight complexing was observed with the metal ions zinc, cobalt and manganese, which is in agreement with potentiometric results. However, with nickel and copper, which were present in equimolar ratio with the ligand, strong complexing was observed. There was a distinct shift of 21 mμ towards the visible when copper ions were present and a 18 mμ shift when nickel ions were present. These results are again in agreement with those obtained potentiometrically, since the formation constants of copper and nickel complexes were found to be 9·48 and 6·94, respectively. It was shown potentiometrically that when the ester of orotic acid was studied as a potential metal complexing agent, little or no complexing was observed. This indicated the important role which the carboxyl group played in the complexing process. Again, to further verify that essentially no complexing occurred, ultra-violet absorption spectra for orotic acid ester and nickel ions were obtained. The results indicated that there was little or no complexing.

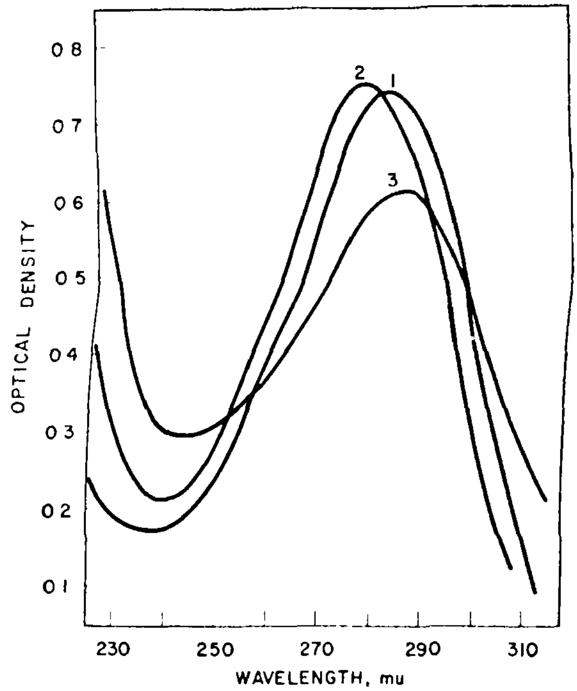


FIG 2 —Ultraviolet absorption spectra of orotic acid in water Curve 1, pH 0 7, 2, pH 6 0, 3, pH 12 0

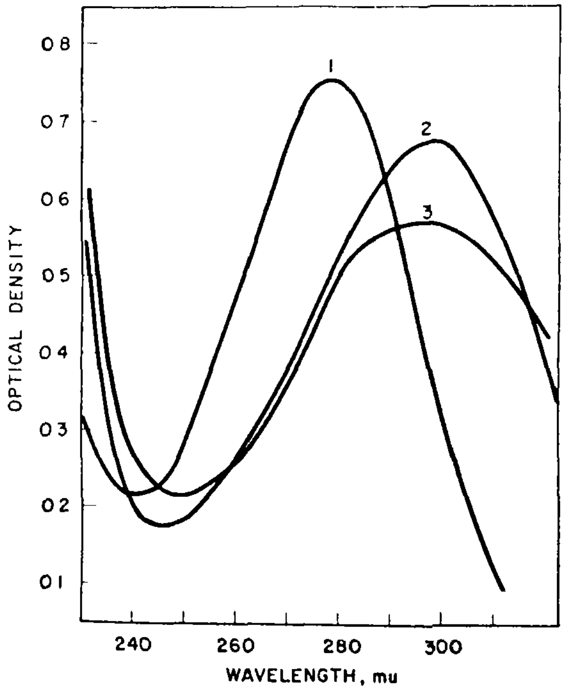


FIG 3 —Ultraviolet absorption spectra of orotic acid containing divalent metal ions in water Curve 1, no metal present, pH 5 0, 2, copper (II), pH 5 0, 3, nickel (II), pH 5 0

Further complex studies of the orotic acid and nickel ions were carried out in a deuterium oxide medium and absorption curves are illustrated in Fig 5 In deuterium oxide the 277 mμ band in orotic acid was shifted to 283 mμ in the presence of nickel (II) ions indicating complex formation However the extent of shift in deuterium oxide was smaller than in water showing that the nickel(II) complex of orotic acid in deuterium oxide is weaker than in water This is reasonable since complexing occurs between the carboxylate ion in the 6-position and the nitrogen in the 1-position with the

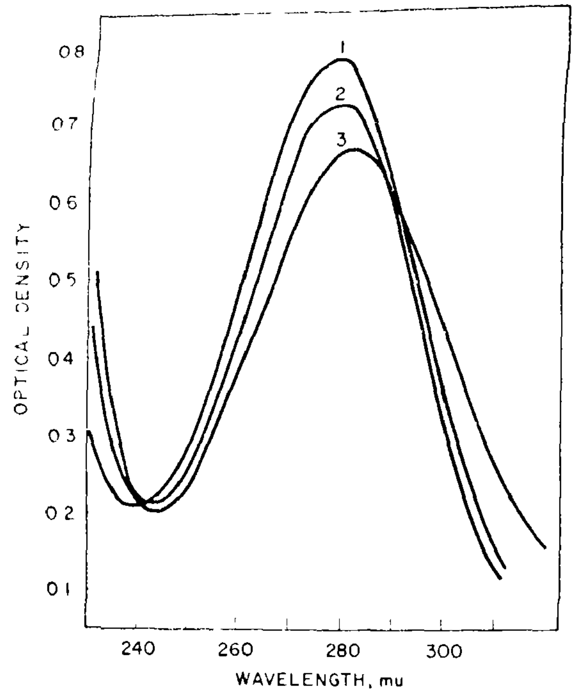


FIG 4 – Ultra-violet absorption spectra of orotic acid containing divalent metal ions in water Curve 1, manganese(II), pH 5 0, 2, cobalt(II), pH 5 0, 3, zinc(II), pH 5 0

proton removed Since the D—N bond cleavage is more difficult to bring about than the H N bond cleavage, one would expect a weakening of the complex in going from water to deuterium oxide

(C) 5-*Nitro-orotic acid spectra*

To determine the effect of a nitro group on orotic acid in metal complexing, ultra-violet light absorption spectra were determined for 5-nitro-orotic acid in water at various pH values with and without metal ions The absorption curves are found in Fig 6 Introduction of a nitro group was found to have a pronounced effect on the dissociation constants determined potentiometrically and also appeared to cause considerable modification of the lactam-lactim equilibria in the pyrimidine nucleus within the high and neutral pH regions Thus, whereas the uracil band in orotic acid was present at 277 mμ at neutral pH, this same band was found to shift to 338 mμ in the same pH region for 5-nitro-orotic acid This shift could be partly attributed to enhanced enolization In the low acid region of pH 0 5, the predominant uracil species is still very likely the ketonic form At pH 12 the wavelength maximum is still 338 mμ,

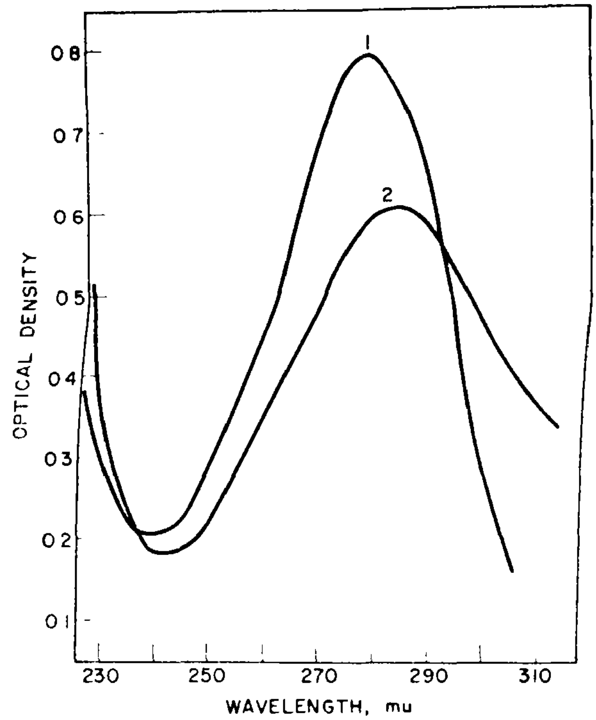


FIG. 5 Ultra-violet absorption spectra of orotic acid containing nickel(II) ion in deuterium oxide Curve 1, no metal present pH 5 0 2, nickel(II), pH 5 0

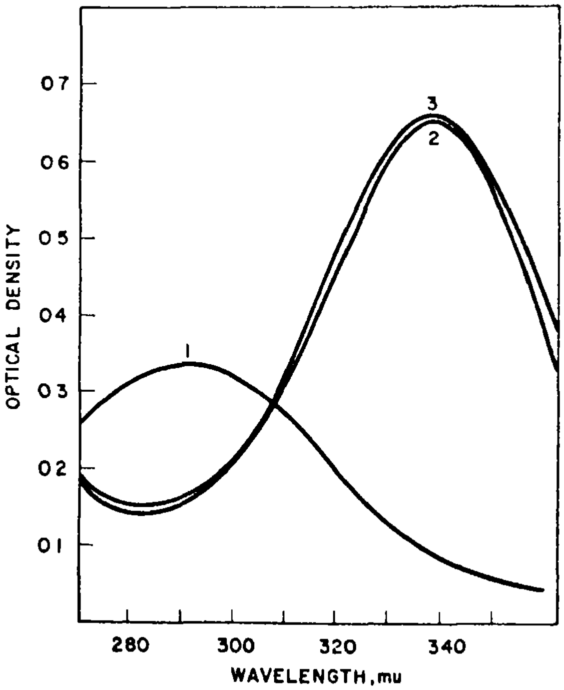


FIG 6—Ultra-violet absorption spectra of 5-nitro-orotic acid in water Curve 1 pH 0 5, 2, pH 7 0, 3, pH 12 0

which indicates that enolization is essentially complete even at pH 7 0 From a consideration of the resonance contributions indicated in the discussion of acid dissociation constants of 5-nitro-orotic acid (5) it follows that enolization would be very favourable in this compound Not only does the probability factor favour enhanced enolization of the 2-position carbonyl group, but also electronic contributions from the nitro group would facilitate enolization

The wavelength maximum as shown in Fig 7, of 5-nitro-orotic acid at pH 1 5 in the presence of copper ion is identical with the maximum at pH 0 5, when no metal ions are present In the low acidic region, complexing would be not expected At pH 6 0 the wavelength maximum in the presence of copper ions is 29 mμ smaller than in the absence of metal, whereas the maximum value is almost independent of the presence of nickel(II) ions As yet we have not been able to explain this curious behaviour except to note that for potentiometric titrations, copper(II) ions also behave abnormally since they appear to remove all the replaceable protons and yet nickel(II) ions do not

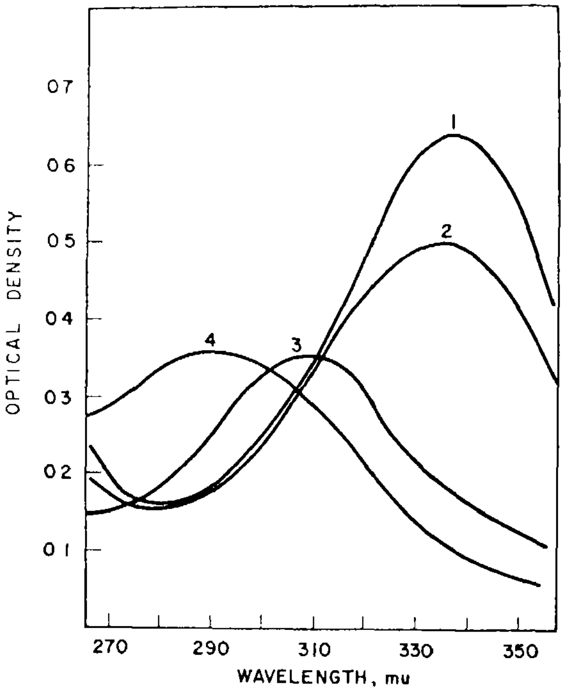


Fig 7 - Ultra-violet absorption spectra of 5-nitroorotic acid containing divalent metal ions in water Curve 1 no metal present pH 6 0, 2 nickel (II), pH 6 0, 3, copper (II), pH 6 0, 4, copper (II), pH 1 5

(D) *2-Ethylthio-iso-orotic acid spectra*

Ultra-violet light absorption spectra were determined for 2-ethylthioiso-orotic acid Substitution of the ethylthio group in the 2-position appears to enhance enolization of the carbonyl group in the 4-position Reference to Fig 8 indicates that at pH 8 0 and 11 0 only one absorption curve is obtained The significance of this occurrence is that at pH 8 0, or perhaps at an even lower pH, enolization of the carbonyl group is nearly complete To further increase the pH would have no observable effect if complete enolization exists. From the absorption curves, this seems to be the case. Again, the fact that enolization may take place at a low pH further substantiates the results obtained from potentiometric investigations of metal complexing. The formation constants of 2-ethylthioiso-orotic acid were found to be lower than those for iso-orotic acid. It was mentioned previously that this was explainable if one considered

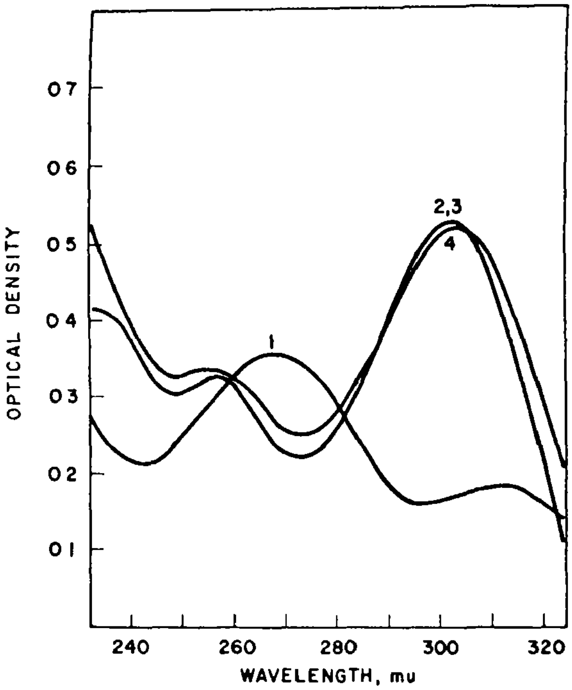


Fig. 8.—Ultra-violet absorption spectra of 2-ethylthio-isoorotic acid in water. Curve 1, pH 1.0; 2, pH 8.0; 3, pH 11.0; 4, copper (II), pH 6.5.

the ethylthio derivative to exist to some extent in the enolic form. Hence the enolic form would complex to a lesser extent with the metal ion through the carboxylate ion than the ketonic form. Spectrophotometric results indicate that the above prediction can actually be observed and the enolic form does exist to a greater extent in the ethylthio derivative than in iso-orotic acid. The ultra-violet absorption spectrum of 2-ethylthioiso-orotic acid with Cu(II) ions present was determined. The metal–ligand solution was adjusted to pH 6.5 and ultra-violet absorption spectrum determined. Although the absorption curve showed complexing of the same order of magnitude as iso-orotic acid, a more significant observation was that even at pH 6.5 the enolic form still appears to predominantly exist.

Acknowledgement—The authors are very grateful to Miss V. KARVEY for assistance in preparation of this manuscript.

J. Inorg Nucl Chem , 1963, Vol 25 pp 29 to 35 Pergamon Press Ltd Printed in Northern Ireland

THE REACTION OF 8-QUINOLINOL WITH COPPER(II) SALTS*

J C Fanning† and H B Jonassen
Department of Chemistry, Tulane University, New Orleans, Louisiana

(Received 19 February 1962, in revised form 18 June 1962)

Abstract – 8-quinolinol (C_9H_6NOH) was reacted with $CuSO_4\,5H_2O$, $Cu(NO_3)_2\,3H_2O$, $CuCl_2\,2H_2O$ $CuCl_2$, $CuBr_2$ $Cu(C_2H_3O_2)_2\,H_2O$ and $Cu(ClO_4)_2\,6H_2O$ The reaction was carried out in both methanol and water at varying concentrations of the copper salts Two forms of $Cu(C_9H_6NO)_2$ were prepared $Cu(C_9H_6NO)X$, where X is Cl or Br, was prepared when halide salts were used These various copper (II) quinolinolates have unusual magnetic and spectral properties

Eight-quinolinol (C_9H_6NOH) produces several different compounds when it reacts with various copper(II) salts The nature of the reaction and the resulting products depend on the anion, solvent, temperature, time and concentration

Suito and Sekido[1] reacted $CuSO_4\,5H_2O$ with C_9H_6NOH in water at various temperatures and concentrations and prepared two forms of $Cu(C_9H_6NO)_2\,2H_2O$

Recently, $CuCl_2$ and $CuBr_2$ have been found to react with C_9H_6NOH to yield the compounds, $Cu(C_9H_6NO)Cl$ and $Cu(C_9H_6NO)Br$, having unusual magnetic properties[2] This reaction can be carried out in a solvent of low dielectric constant or at high salt concentrations in water

In order to investigate the reaction further, C_9H_6NOH was reacted in water and methanol with the following salts $Cu(ClO_4)_2\,H_2O$, $Cu(NO_3)_2\,3H_2O$, $Cu(C_2H_3O_2)_2\,H_2O$, $CuSO_4\,5H_2O$, $CuCl_2\,2H_2O$, $CuCl_2$, and $CuBr_2$ Since the basic nature of the anion seems to play an important part in the reaction, the reactions in methanol were carried out at varying concentrations of NaOH

EXPERIMENTAL

Materials

Anhydrous methanol was prepared by the method of Vogel[3]

$CuCl_2$ was prepared by heating at about 150 C $CuCl_2\,2H_2O$ in an HCl atmosphere $CuBr_2$ was prepared by the action of excess HBr on $CuCO_3$ and recrystallization of the product $Cu(ClO_4)_2\,6H_2O$ was obtained from the G Frederick Smith Chemical Co All other metal salts were J P Baker's Analysed Reagent' grade

Analysis

The C, H, N, and halogen analysis were carried out by A Bernhardt Microanalytical Laboratories Mulheim, Germany Copper was determined electrolytically after decomposing the complexes in mixtures of HNO_3, H_2SO_4 and $HClO_4$[4] C_9H_6NOH was analysed spectrophotometrically as the hydrochloride according to the method reported by Hollingshead[5]

---

* Presented in part at the Southwide American Chemical Society Meeting in New Orleans, Louisiana December 7 9, 1961

† Department of Chemistry and Geology, Clemson College, Clemson, South, Carolina

[1] E Suito and F Sekido, *Proc Japan Acad* 33, 196 (1957)

[2] J C Fanning and H B Jonassen, *Chem and Industr* 1623 (1961)

[3] J Vogel, *Textbook of Practical Organic Chemistry*, p 168 Longmans, Green, London (1951)

[4] I M Kolthoff and E B Sandell, *Textbook of Quantitative Inorganic Analysis* p 407 Macmillan, New York (1952)

[5] R G W Hollingshead, *Oxine and Its Derivatives*, Vol 1, p 49 Butterworths, London (1954)

Preparation of copper quinolinolates

A. $Cu(C_9H_6NO)_2 \cdot 2H_2O$. To a suitable volume of an aqueous copper(II) salt solution with known concentration was added a slightly less than equivalent amount of C_9H_6NOH as a 5 per cent ethanol solution. After standing for about a week the precipitate was filtered, washed with H_2O, and dried at room temperature in a desiccator. (Found: Cu, 16.72; C_9H_7NO, 74.5; H_2O, 9.17. Calc. for $Cu(C_9H_6NO)_2 \cdot 2H_2O$: Cu, 16.38; C_9H_7NO, 74.35; H_2O, 9.29%.)

B. *Preparation of* $Cu(C_9H_6NO)_2$. Part of the precipitate was placed in an oven and dried at 110°C to constant weight. (Found: Cu, 18.10. Calc. for $Cu(C_9H_6NO)_2$: Cu, 18.06%.)

C. *Preparation of* $Cu(C_9H_6NO)_2$ (α). Fifty ml of a 0.1F solution of $Cu(C_2H_3O_2)_2 \cdot H_2O$ in methanol was added to 100 ml of 0.1F C_9H_6NOH. A precipitate formed immediately which was filtered off, washed with several portions of methanol and dried at 110°C. (Found: Cu, 18.15; C_9H_7NO, 81.6. Calc. for $Cu(C_9H_6NO)_2$ (α): Cu, 18.06; C_9H_7NO, 81.98%.)

D. *Preparation of* $Cu(C_9H_6NO)_2$ (β). Fifty ml of a 0.1F solution of $Cu(C_2H_3O_2)_2 \cdot H_2O$ in methanol was added to 100 ml of 0.1F C_9H_6NOH. The precipitate was allowed to stand in solution for at least two days. The solid was then filtered off and washed with several portions of methanol and dried at 110°C. (Found: Cu, 18.07; C_9H_7NO, 81.8. Calc. for $Cu(C_9H_6NO)_2$ (β): Cu, 18.06; C_9H_7NO, 81.98%.)

E. *Conversion of* $Cu(C_9H_6NO)_2$ (α) *to* $Cu(C_9H_6NO)_2$ (β). Table 1 shows the results of the reaction carried out in methanol with and without hydroxide ion. The concentration of the copper(II) salts was 0.1F. Two different 0.1F solutions of C_9H_6NOH were prepared—to one was added enough NaOH to make the solution 0.015F in NaOH. The solids obtained were washed with several portions of methanol and dried at 110°C. The change from the α form to the β form was carried out by allowing the $Cu(C_9H_6NO)_2$ (α) to remain in solution.

TABLE 1.—REACTIONS IN METHANOL

Salt	[NaOH] = 0	[NaOH] = 0.015F
$Cu(ClO_4)_2 \cdot 6H_2O$	$Cu(C_9H_6NO)_2$ (β) after 3–4 days—green solution	Green solution No precipitate
$Cu(NO_3)_2 \cdot 3H_2O$	$Cu(C_9H_6NO)_2$ (β) after 2–3 hr—green solution	Green solution No precipitate
$Cu(C_2H_3O_2)_2 \cdot H_2O$	$Cu(C_9H_6NO)_2$ (α) immediately $Cu(C_9H_6NO)_2$ (β) after 2 hr green solution	$Cu(C_9H_6NO)_2$ (β) after 1 day—green solution
$CuSO_4 \cdot 5H_2O$	$Cu(C_9H_6NO)_2$ (α) immediately $Cu(C_9H_6NO)_2$ (β) after 1 day green solution	Green solution fine white precipitate ($CuSO_4$)
$CuCl_2 \cdot 2H_2O$	$Cu(C_9H_6NO)Cl$ immediately	$Cu(C_9H_6NO)Cl$ immediately
$CuCl_2$	$Cu(C_9H_6NO)Cl$ immediately	$Cu(C_9H_6NO)Cl$ immediately
$CuBr_2$	$Cu(C_9H_6NO)Cl$ immediately	$Cu(C_9H_6NO)Cl$ immediately

Studies of physical properties

The density of the solids in Table 2 were determined by a flotation method employing mixtures of dihalogenated alkanes.[6]

The influence of heat on the samples was studied with a Fisher-Johns Melting Point Apparatus. The results are given in Table 2.

The magnetic susceptibilities were obtained on a Gouy balance at room temperature. They have been corrected using Pascal's constants.[7]

---

[6] R. E. DODD and P. L. ROBINSON, *Experimental Inorganic Chemistry*, p. 357. Elsevier, London, (1957).

[7] G. FOEX, C. J. GORTER and L. J. SMITS, *Constantes Selectionnees Diamagnetisme et Paramagnetisme*, Masson et Cie, Paris (1957).

TABLE 2.—PROPERTIES OF THE SOLIDS

Solid	Colour	Density (g/ml)	Effect of heat	9 μ peak (cm^{-1})	Reflectance spectra peaks (mμ)	χ_m × 10^6 (emu/mole)	Magnetic properties	
							T(°C)	μ (B.M.)
$Cu(C_9H_6NO)_2$ (α)	Bronze	1.48	210°C—changes to β	1118	See Fig. 1	1565	25	1.95
$Cu(C_9H_6NO)_2$ (β)	Black, bronze when crushed	1.43	269°C—decomposes	1111	See Fig. 1	1310 1406	27 24	1.73 (crushed) 1.83 (crystalline)
$Cu(C_9H_6NO)_2 \cdot 2H_2O$	Yellow-green	--	28°C—begins to lose H_2O	1109	ca. 350 660	1529	28	1.92
$Cu(C_9H_6NO)Cl$	Tan	1.71	301°C decomposes	1114	375 810–850	318	25	0.95
$Cu(C_9H_6NO)Br$	Red-brown	2.24	260°C decomposes	1111	395 800–890	510	24	1.10

The infra-red spectra were obtained on a Beckman IR5 having NaCl optics. The Nujol mull method employed by FREISER and his co-workers[8] was used in a few cases. Hexachlorobutadiene mulls were used to compliment the Nujol spectra. The infra-red data is given in Table 3.

The reflectance spectra were obtained on a Beckman DU using the reflectance attachment. $MgCO_3$

TABLE 3.—INFRA-RED SPECTRA

(C_9H_7NO)*	$Cu(C_9H_6NO)_2$ (α)†	$Cu(C_9H_6NO)_2$ (β)‡	$Cu(C_9H_6NO)_2$ $2H_2O$	$Cu(C_9H_6NO)Cl$	$Cu(C_9H_6NO)Br$
	640(*m*)	639(*m*)	635(*m*)	632(*s*)	631(*s*)
		653(*w*)			
709(*s*)					
	721(*vs*)				
		730(*s*)			
740(*s*)	744(*s*)	758(*vs*)	744(*vs*)	743(*vs*)	743(*vs*)
	750(*m*)			750(*vs*)	
780(*s*)	785(*vs*)	778(*vs*)	781(*s*)	785(*s*)	780(*s*)
		794(*s*)	788(*s*)	800(*sh w*)	
805(*sh m*)	804(*s*)	804(*s*)	805(*m*)	808(*m*)	807(*m*)
815(*m*)	819(*vs*)	815(*s*)	818(*s*)	819(*vs*)	820(*s*)
		827(*s*)			
		833(*s*)			
	850(*w*)	851(*m*)	855(*m*)		
863(*w*)				877(*w*)	875(*w*)
895(*m*)	925(*w*)		915(*m*)	917(*w*)	915(*w*)
	943(*w*)		952(*w*)		948(*w*)
	946(*w*)	947(*w*)		946(*w*)	
9[illegible]0(*w*)	960(*w*)	965(*w*)		960(*w*)	
	977(*w*)		975(*w*)	985(*w*)	
1011(*w*)	1031(*m*)	1031(*m*)	1033(*m*)	1032(*w*)	1035(*w*)
1055(*m*)		1050(*w*)	1065(*w*)	1057(*w*)	
				1065(*w*)	
1090(*m*)	1118(*s*)	1111(*vs*)	1109(*vs*)	1114(*vs*)	1111(*vs*)
1130(*w*)	1130(*w*)		1135(*w*)	1139(*w*)	1135(*w*)
	1148(*m*)				
1165(*m*)					
1170(*sh m*)	1177(*m*)	1170(*w*)	1177(*w*)	1173(*m*)	1175(*w*)
1200(*s*)		1210(*sh m*)	1203(*w*)	1213(*w*)	1210(*w*)
1220(*s*)	1222(*m*)	1220(*s*)	1227(*m*)		
	1232(*m*)	1230(*s*)		1235(*m*)	1235(*w*)
1275(*s*)		1275(*s*)		1267(*s*)	1270(*vs*)
1280(*s*)	1280(*s*)		1282(*m*)		
	1320(*s*)	1320(*vs*)	1320(*s*)	1315(*vs*)	1315(*vs*)
1380(*s*)	1370(*vs*)	1370(*vs*)	1370(*vs*)†	1375(*vs*)	1375(*vs*)
			1390(*vs*)	1390(*sh s*)	
1400(*s*)	1410(*sh w*)	1415(*sh m*)	1420(*m*)	1420(*m*)	1420(*m*)
1430(*m*)	1430(*sh m*)	1430(*sh s*)			
1470(*m*)	1460(*vs*)	1455(*vs*)	1455(*vs*)†	1460(*vs*)	1460(*vs*)
1500(*s*)	1500(*vs*)	1490(*s*)	1495(*vs*)	1498(*vs*)	1500(*vs*)
1580(*m*)	1570(*s*)	1560(*s*)	1560(*s*)	1575(*s*)	1570(*s*)
	1590(*m*)	1590(*m*)	1590(*m*)	1600(*m*)	1600(*m*)
			1610(*m*)		
1740(*w*)					
1900(*w*)					
			2840} band	2840(*w*)	2840(*w*)
3100} band			3010} (*m*)	2910(*w*)	2900(*w*)
3300} (*s*)			3320(*m*)	3030(*m*)	3020(*w*)

vs-very strong, *s*-strong, *m*-medium, *sh*-shoulder, *w*-weak

* KBr disc

† Combined spectra from Nujol and hexachlorobutadiene mulls

‡ Possibly Nujol peaks

---

[8] R G CHARLES, H FREISER, R FRIDEL, L H HILLIARD and W D JOHNSTON, *Spectrochim Acta* **8**, 1 (1956)

was used as a standard Fig 1 gives the reflectance spectra for $Cu(C_9H_6NO)_2$(α) and (β) forms The β spectra is given for both the crystals and crushed material The β crystals were crushed with an agate mortar and pestle

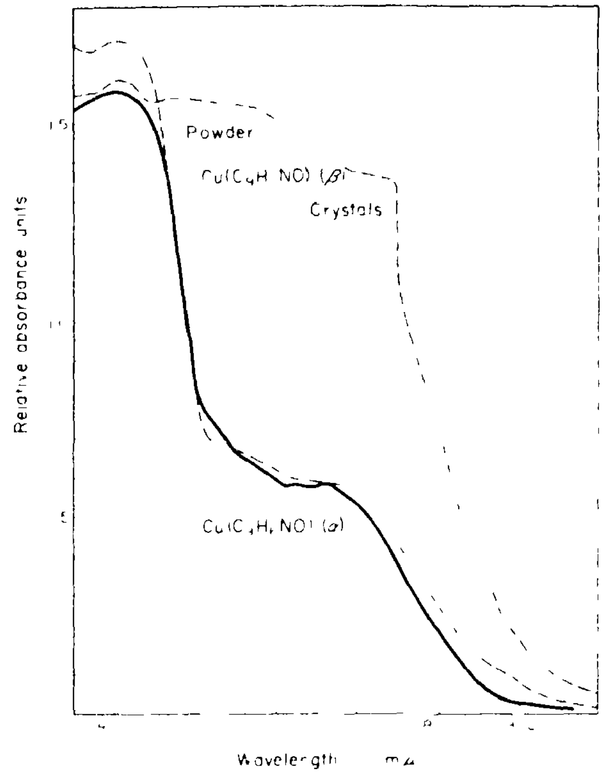


FIG 1

DISCUSSION AND RESULTS

In methanol the formation of the α and β forms of $Cu(C_9H_6NO)_2$ seems directly related to the nature of the anion The presence of NaOH prevents or delays the appearance of $Cu(C_9H_6NO)_2$ To interpret this reaction both the basicity of the anion and its coordinating tendency must be considered

As the conditions described in Table 1 show those copper(II) salts containing non-co-ordinating weakly basic anions (ClO_4^-, NO_3^-) give the β form only

On the other hand those copper(II) salts containing basic anions (acetate, sulphate) which form fairly stable complexes ($Cu(C_2H_3O_2)_2$ $K = 5 \times 10^{-4}$ $CuSO_4$ $K = 4.5 \times 10^{-3}$)(9) precipitate as the α-form

This might indicate that under these conditions the first reaction is the displacement of the ligand from one or more positions because of the reaction of the proton of C_9H_6NOH with the ligand to give $HC_2H_3O_2$ for example This could lead to a mixed complex such as, $[Cu(C_2H_3O_2)C_9H_6NO)]$

A process of this type had been shown to be present in the formation of the mixed complexes $Cu(C_9H_6NO)Cl$ and $Cu(C_9H_6NO)Br$ (2)

A second C_9H_6NOH can then react with the mixed ligand species to give the form of $Cu(C_9H_6NO)_2$

---

(9) K B YATSIMIRSKII and V P VASIL'EV, *Instability Constants of Complex Compounds* (English Translation) p 149, p 125 Pergamon, Oxford (1960)

On the other hand in basic solution (Table 1) where an appreciable concentration of the basic $C_9H_6NO^-$ anion is present the reaction leads slowly to the β-form of the $Cu(C_9H_6NO)_2$ at least for $Cu(C_2H_3O_2)_2$. A detailed study of the effect of pH and other variables on the formation of β-form from $Cu(C_2H_3O_2)_2$ and $CuSO_4$ will be published elsewhere.(10)

When Cu(II) salts react in aqueous solution with C_9H_6NOH the precipitate is $Cu(C_9H_6NO)_2 \cdot 2H_2O$. Depending on the reaction conditions under which $Cu(C_9H_6NO)_2 \cdot 2H_2O$ was formed either the α- or the β-form of $Cu(C_9H_6NO)_2$ can be formed when the hydrate is heated. These observations are in line with those of SUITO and SEKIDO.(1)

Although X-ray powder patterns showed two forms of $Cu(C_9H_6NO)_2 \cdot 2H_2O$, the infra-red spectra of the two species are the same. For the α- and β-forms of $Cu(C_9H_6NO)_2$ however powder patterns and infra-red spectra are different.

In Fig. 1 the reflectance spectra of the α- and β-forms are shown. The hard, black β-crystals give a different reflectance curve than the α-form, however, upon grinding the β-form takes on the colour and reflectance characteristics of the α-form. Furthermore upon heating at about 200°C the β-crystals "pop" open and produce the colour characteristics of the α-form even though the infra-red characteristics remain the same.

It was thought that the difference in reflectance characteristics of these two forms might be due to the occlusion of oxygen. The same two forms could, however, be obtained under a nitrogen blanket.

X-ray patterns of the crushed material and of the crystals are identical.(11)

The magnetic properties of both the crushed and crystalline $Cu(C_9H_6NO)_2$ (β) were measured. A real difference was found which however may be due to the possible non-uniformity of the crystalline material in the sample tube.

The infra-red spectra of the α- and β-forms show considerable difference. The only peak which has been characterized is the "9 μ" peak. This peak in the vicinity of 9 μ (1090 cm^{-1} for C_9H_6NOH) has been assigned to the aryl-oxygen vibration in the C_9H_6NOH.(5) Infra-red spectra of a large number of metal C_9H_6NOH complexes have been measured. The exact position of the 9μ peak in cm^{-1} was plotted as a function of the atomic weight of the metal and two straight lines resulted. One line contained the metal complexes of Mg(II), Ca(II), Zn(II), Cd(II) and Pb(II). The other line included Cu(II), Ni(II), and Mn(II). Co(II) was at the intersection of the lines. The Cu spectra used in Reference (5) was, upon comparison, that of the α-form. The β-form would be at a position close to the first line.

It has been suggested that the complexes lying along each line may have structural similarity. Only one, $Zn(C_9H_6NO)_2$, is known to be tetrahedral.(12) $Cu(C_9H_6NO)_2$ (α) may be similar in structure to the Ni and Mn chelates. On the other hand $Cu(C_9H_6NO)_2$ (β) may be a structural intermediate between its α-form and the group made up of Mg, Ca, Zn, etc.

If the magnetic moment difference is considered, the α-complex should be tetrahedral and the β-complex, planar.(13)

---

(10) J. KYRKI and H. B. JONASSEN, *Acta Chem. Scand.* To be submitted.

(11) A. J. BERTRAND. Unpublished results.

(12) J. C. LIU and J. C. BAILAR, *J. Amer. Chem. Soc.* **73**, 5432 (1951).

(13) K. ITO and T. ITO, *Aust. J. Chem.*, **11**, 406 (1958).

When an aqueous solution of $CuCl_2$ with a formality greater than 0 062 reacts with C_9H_6NOH only $Cu(C_9H_6NO)Cl$ forms This occurs at even lower concentration of $CuCl_2$ if excess chloride ions are added Under similar conditions the corresponding $Cu(C_9H_6NO)Br$ is formed Their properties have been discussed in a previous paper (2) Their properties are listed again in order to compare them with the other complexes Further studies on these complexes are in progress

Acknowledgement Appreciation is extended to some members of the Chemistry Honour Class of 1960 61 of Tulane University for their interest and their assistance in making many of the measurements Dr E A BOUDREAUX's aid in making the magnetic measurements is acknowledged This work was supported in part by the Office of Naval Research

J. Inorg. Nucl. Chem. 1963, Vol. 25, pp. 37 to 44. Pergamon Press Ltd. Printed in Northern Ireland

THERMAL DECOMPOSITION OF THE TRIS (2,2′-BIPYRIDINE) COMPLEXES OF SOME FIRST ROW TRANSITION GROUP ELEMENTS IN THE SOLID STATE

S. K. DHAR* and F. BASOLO
Contribution from the Chemical Laboratories of Northwestern University,
Evanston, Illinois

(*Received* 4 *April* 1962; *in revised form* 6 *June* 1962)

Abstract—Kinetics of the isothermal solid state decomposition of the tris (2,2′-bipyridine) complexes of the first row transition group elements $[M(bipy)_3]Br_2$† ($M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}$ and Zn^{2+}) were studied under vacuum using a weight loss method. Decomposition of $[Fe(bipy)_3]Br_2$, $[Ni(bipy)_3]Br_2$ and $[Cu(bipy)_3]Br_2$ were found to obey the Prout and Tomkins' rate equation, $d\alpha/dt = k\alpha(1 - \alpha)$. For the rest of the compounds the data were not reproducible enough to permit a definite conclusion. The activation energies for the first dissociation step of the complexes of Fe^{2+}, Ni^{2+} and Cu^{2+} are given as is also a study of their decomposition products.

AN attempt was made to study the thermal decomposition of the compounds $[M(bipy)_3]Br_2$, where $M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}$ and Zn^{2+}, in solid state. The initial objective of this study was to determine the activation energies for the solid state dissociations of these complexes in order to see if they correlate the crystal field energies operative in such a series.

The present study indicates that the decomposition process takes place by complex mechanisms critically dependent on the characteristics of the solid. These in some cases, are apparently not reproducible. For $M = Fe^{2+}$ and Ni^{2+} the data are fairly consistent. The same is almost true for the Cu^{2+} compound. For corresponding compounds of Mn^{2+}, Co^{2+}, and Zn^{2+} the data are not reproducible.

In a solid state decomposition of the type $A_s \rightarrow B_s + C_g$, the onset of reaction involves the formation of a new phase B at special points in the lattice of A. Local deformation of the lattice must occur to cause this, which is referred to as "strain". The potential nucleus sites are generally associated with some types of lattice imperfection, for example lattice defects, dislocations, Smekel cracks, etc.(1) Therefore the rate of decomposition, dependent on the rate of nucleus formation, is a function of the particular crystal structure and surface condition of the solid sample. A number of mechanisms have been postulated(2) to account for such decompositions but an apparent agreement with one or the other rate equations does not necessarily prove the mechanism.(3)

The rate equation which was found primarily applicable in this study is due to PROUT and TOMPKINS(4). It is given by $d\alpha/dt = k\alpha(1 - \alpha)$ where k is the probability of branching of the nuclei chain and is assumed constant x is the fraction decomposed at time t The energy of activation data were calculated from the Arrhenius equation

---

* Present address: Argonne National Laboratory, Argonne, Illinois.

† bipy = 2,2′-bipyridine.

(1) W. E. GARNER (Editor) *Chemistry of the Solid State* p. 187. Butterworth, London (1955).

(2) W. E. GARNER (Editor) *Chemistry of the Solid State*, Chap. 7. Butterworth, London (1955).

(3) W. E. GARNER (Editor) *Chemistry of the Solid State*, p. 206. Butterworth, London (1955).

(4) E. G. PROUT and F. C. TOMPKINS, *Trans. Farad. Soc.* **40**, 488 (1944).

RESULTS AND DISCUSSION

Tris (2 2 -bipyridine)iron(II) bromide pentahydrate The isothermal decomposition of this compound in the temperature range 168 177 gives a product analytically approximating $Fe(bipy)_{1\ 5}Br_2$ (Table 2) The energy of activation of the decomposition step $[Fe(bipy)_3]Br_2 \rightarrow Fe(bipy)_{1\ 5}Br_2$ 1 5 bipy is 75 kcal mole^{-1} with an estimated maximum slope variation of 5% (Table 3 and Fig 3) The associated water molecules are assumed to be lost in the prerecorded decomposition step Another possibility is that the water may be lost only as a consequence of the decomposition of the complex and thus be of secondary significance This is also generally true for the rest of the compounds except $[Mn(bipy)_3]Br_2$ which was anhydrous to start with The decomposition product is light pink compared to the dark pink colour of the tris compound and dull red colour of the mono compound, $[Fe(bipy)Br_2]$ The product may be formulated principally as $[Fe(bipy)_3][FeBr_4]$ In support of this assumption are the magnetic moment (5 45 B M) and molar conductivity (43, 182 and 275 in nitrobenzene, nitromethane and acetonitrile, respectively) of the compound The magnetic moment of the $[FeBr_4]^{2}$ ion is given to be 5 4 B M (5) and that of the tris compound is approximately nil The observed value of 5 45 for $[Fe(bipy)_{1\ 5}Br_2]_2$ is thus in excellent agreement with the above formulation The reflectance spectra provides additional support The spectrum of $[Fe(bipy)Br_2]$ indicates a broad absorption band around 1050 mμ (Fig 4) which is absent in those of $[Fe(bipy)_3]Br_2\ 5H_2O$ and $Fe(bipy)_{1\ 5}Br_2$ This observation therefore tends to rule out alternate formulations such as $[Fe(bipy)Br_2]$ 0 5 bipy or $[Fe(bipy)Br_2]$ $[Fe(bipy)_2Br_2]$

Earlier work showed the isothermal decomposition product of $[Fe(bipy)_3]Cl_2$ at 100 to be the bis compound (6) The anion thus makes a significant difference in the decomposition steps of these compounds The same behaviour is observed in the decomposition of the corresponding nickel complex

Tris (2 2'-bipyridine)nickel(II) bromide pentahydrate The decomposition product of this compound obtained in the range of 189 5 -203 5 also analytically approximates $Ni(bipy)_{1\ 5}Br_2$ (Table 2) The reaction rate constant values (branching coefficient) are reproducible within ± 5 per cent The Arrhenius energy of activation is 56 kcal mole^{-1} with an estimated maximum slope variation of 10 per cent (Table 3) The reaction product is again assumed to be $[Ni(bipy)_3][NiBr_4]$ as with the iron(II) complex In support of this formulation are the molar conductivity (308 in CH_3CN), magnetic moment and reflectance spectrum (Fig 5) of the decomposition product

The observed magnetic moment of 3 4 B M per nickel ion agrees well with the expected value of 3 46 for the formulation $[Ni(bipy)_3][NiBr_4]$ arrived at by taking the geometric mean of the magnetic moments of the individual ions (7-9) Although the reflectance spectrum of the thermal product does not show the double peak of the $[NiBr_4]^{2}$ ion,(10) the spectrum is characterized by a pronounced absorption band at

---

(5) N S GILL *J Chem Soc* 3512 (1961)

(6) F BASOLO and F P DWYER, *J Chem Soc* **76,** 1454 (1954)

(7) F H BURSTALL and R S NYHOLM, *J Chem Soc* 3570 (1952)

(8) N S GILL and R S NYHOLM, *J Chem Soc* 3997 (1959)

(9) C M HARRIS and E D MCKENZIE, *J Inorg Nucl Chem* **19,** 372 (1961)

(10) F A COTTON and R FRANCIS, *J Inorg Nucl Chem* **17,** 62 (1961)

~725 mμ (Fig 5) This serves as a good indication of the presence of the tetrabromo ion Such a band does not occur in either the tris or the bis compound A synthetic sample of $[Ni(bipy)_3][NiBr_4]$ was prepared by mixing equimolar amounts of $[Ni(bipy)_3]Br_2$ $5H_2O$ and $[N(C_4H_9)_4]_2[NiBr_4]$ *in acetonitrile, and precipitating the desired salt by adding excess diethyl ether The reflectance spectrum of this compound is in close agreement with that of the thermal product* (Fig 5)

Tris (2,2′-*bipyridine*)*copper*(II) *bromide monohydrate* Since the third bipyridyl group is held relatively loosely in this compound the initial vacuum equilibration was done by jacketing the sample tube in a cold bath at 10 After proper

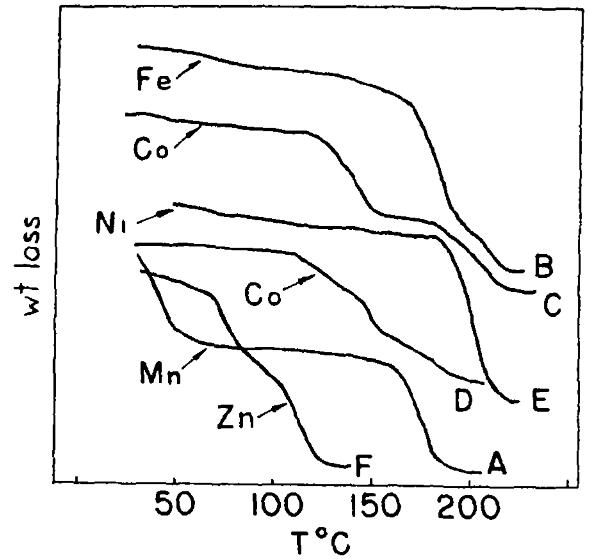


Fig 1 Thermograms of $[M(bipy)_3]Br_2$ nH_2O
A $[Mn(bipy)_3]Br_2$ B $[Fe(bipy)_3]Br_2$ $5H_2O$
C $[Co(bipy)_3]Br_2$ $5H_2O$ D $[Co(bipy)_3]Br_2$ ~2 $5H_2O$
E $[Ni(bipy)_3]Br_2$ $5H_2O$ F $[Zn(bipy)_3]Br_2$ $4H_2O$

vacuum was attained the temperature was rapidly raised to the desired level The isotherms were marked by pronounced induction periods (Fig 2) which were often not reproducible The rate constant values also fluctuated somewhat between different

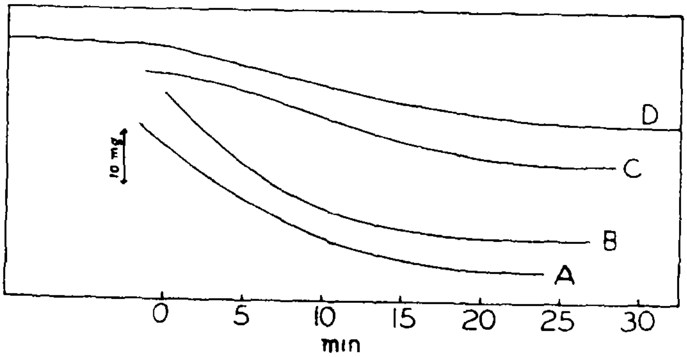


Fig 2 - Isotherms of $[M(bipy)_3]Br_2$ nH_2O
A $[Fe(bipy)_3]Br_2$, 171 0 C B $[Ni(bipy)_3]Br_2$, 193 5 C
C $[Cu(bipy)_3]Br_2$, 50 5 C D $[Mn(bipy)_3]Br_2$ 47 4 C

samples, although the energy of activation determined on three individual batches were concurrent (Table 3). The decomposition product is [Cu(bipy)$_2$Br$_2$]. The thermogram indicates a second dissociation step to [Cu(bipy)Br$_2$] at a higher temperature. This was not further investigated.

Tris (2,2′-*bipyridine*)*cobalt*(II) *bromide hydrate*. The thermograms of this compound shows two broad patterns (Fig. 1). The isotherms also differed from batch to batch and so do the decomposition products. The rate equations followed were likewise not consistent. In addition to the PROUT and TOMPKINS[3] equation, the unimolecular rate equation $\log(1-\alpha) = -kt + c$ was also found to hold for a particular batch. A more thorough study is desirable in conjunction with a structural investigation to probe into this discrepancy.

Tris (2,2′-*bipyridine*)*manganese*(II) *bromide*. No consistent rate constant could be obtained with this compound. The isotherms are characterized by pronounced and irreproducible induction periods which largely vitiate the rest of the isotherm. The compound dissociates in two steps. This is similar to the corresponding copper and zinc complexes which also yield the bis and mono complexes (Fig. 1). No attempts were made to study the kinetics of the second step.

Tris (2,2′-*bipyridine*)*zinc*(II) *bromide tetrahydrate*. This compound presents an interesting example of the variation in isothermal decomposition mechanism on aging. A freshly prepared sample gave isotherms following the rate equation $\log[\alpha/(1-\alpha)] = \log kt + c$. The same sample after standing for ten days in a closed vial gave an isotherm in agreement with the original PROUT and TOMPKINS equation. However, one of the fresh batches also gave an isotherm corresponding to the Prout and Tompkins equation and an activation energy of ~33 kcal mole^{-1}. Although this value seems reasonable, no reliance can be placed on it because of the difficulties encountered.

That the highest activation energy observed was for the decomposition of [Fe(bipy)$_3$]Br$_2$ is consistent with its spin paired configuration. The higher incipient decomposition temperature for [Ni(bipy)$_3$]Br$_2$ on the other hand would mean a considerably lower entropy factor for the nickel complex in comparison to that of the iron(II) compound. This observation also points out the risk of correlating incipient decomposition temperature observed in thermogravimetry to any fundamental property such as stability of the compound. However, it is of interest to note that such a less favourable entropy term for the dissociation of these nickel (II) complexes relative to the iron(II) compounds was also observed for their reactions in aqueous solution.[11] The lowest value observed for [Cu(bipy)$_3$]Br$_2$ indicates a greater stability of the square planar or tetragonal bisbipyridyl complex compared to the tris form. Recent data by CABANI *et al.*[12] gave $\log k_1$, $\log k_2$ and $\log k_3$ values for this complex as 8.47, 5.58 and 3.51 respectively. The observed value of activation energy for the dissociation of the tris compound is thus consistent with the thermodynamic stabilities of the bis and the tris forms. The overall dissociation constant for [Fe(bipy)$_3$]Br$_2$ is given in the range of 10^{-17},[13] and $\log k_1$, $\log k_2$ and $\log k_3$ values for the nickel compound are known now from the recent data of Cabani and Landucci to be 6.9, 6.8, and 5.9 respectively.[15]

The incipient decomposition temperature of [Mn(bipy)$_3$]Br$_2$ and [Zn(bipy)$_3$]Br$_2$ at

---

[11] F. BASOLO, J. C. HAYES and H. M. NEUMANN, *J. Amer. Chem. Soc.* **76**, 3807 (1954).

[12] S. CABANI, G. MORETTI and F. SCROCCO, *J. Chem. Soc.* 88 (1962).

[13] J. BJERRUM, G. SCHWARZENBACH and L. G. SILLEN, *Stability Constant* Part I, p. 70. The Chemical Society, London (1957).

25° and 65° (Fig 1), respectively, suggests a lower order of stability for both than for the corresponding iron(II) and nickel (II) systems Such a results is consistent with the known thermodynamic stabilities for these systems (14,15) However, in the absence of reliable activation energy values such a correlation is not necessarily justified

EXPERIMENTAL

Kinetic measurements A preliminary estimate of the decomposition pattern of the compounds was obtained through their thermograms run under vacuum The vacuum was necessary to ensure removal of the free bipyridine formed as a reaction product A finely ground sample (150 mesh)

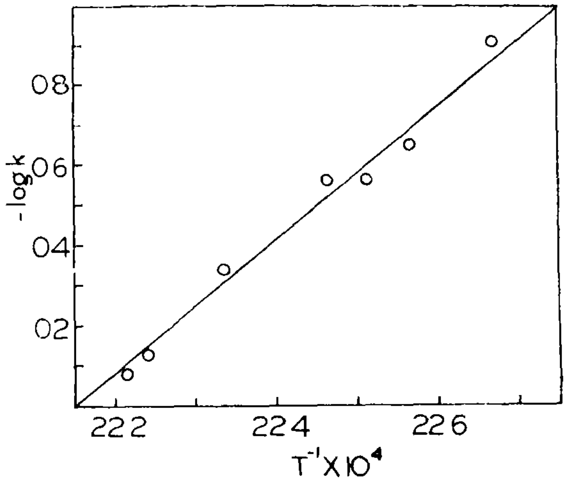


FIG 3 - Arrhenius activation energy plot of the decomposition step
2[Fe(bipy)$_3$]Br$_2$ → [Fe(bipy)$_3$][FeBr$_4$] + 3 bipy

approximately 100 mg in weight, was placed in the sample holder in the form of a thin layer and its surface was furrowed to expose maximum surface area The balance housing, after introduction of the sample was evacuated to a constant vacuum of 600 μ and the preheated furnace was then positioned around the sample tube The isothermal kinetics was recorded after temperature equilibrium was attained This led to partial decomposition of the sample prior to the actual recording The equation, $\ln[\alpha/(1-\alpha)] = kt + c$, used to treat the data predicts a decrease of the rate constant with increasing sample weight A qualitative experimental verification of this was obtained as is shown in Table 1 The sample quantity and recording of isotherms were therefore so regulated as to give

TABLE 1 —EFFECT OF SAMPLE WEIGHT ON THE RATE CONSTANT FOR THE REACTION
Ni(bipy)$_3$Br$_2$ → Ni(bipy)$_{1.5}$Br$_2$ + 1.5 bipy

Temp (°C)	Sample weight (mg)	Recorded weight loss (mg)	Reaction rate constant (min^{-1})
189.5	60	18.5	0.122
189.5	100	33	0.0965
196.5	60	14.7	0.37
196.5	80	22	0.31
196.5	100	28	0.282

reasonably close residual sample weight for each set of experiments For [Fe(bipy)$_3$]Br$_2$, [Ni(bipy)$_3$]Br$_2$ and [Cu(bipy)$_3$]Br$_2$, the recorded weight loss values were in the range of 22-19, 24-22, and 17-15

---

(14) R R MILLER and W BRANDT, *J Amer Chem Soc* 77, 1384 (1955)
(15) S CABANI and M LANDUCCI, *J Chem Soc* 278 (1962)

Accession number
38975

mg respectively. *The probable error from this fluctuation is expected to be well within the experimental reproducibility of ±6 per cent as is evident from Table 1. This was also borne out experimentally.*

Under the conditions employed the best fit of the experimental data was obtained using the equation proposed by Prout and Tompkins(4). The isotherms were found to show an autocatalytic behaviour; the extent of autocatalysis was extensive and irreproducible for the lower temperature decompositions of $[Mn(bipy)_3]Br_2$, $[Cu(bipy)_3]Br_2 \cdot H_2O$ and $[Zn(bipy)_3]Br_2 \cdot 4H_2O$. In addition to the Prout and Tompkins equation the unimolecular rate equation $\log(1-\alpha) = kt + c$ and the equation $\log[\alpha/(1-\alpha)] = \log kt + c$ were occasionally observed to give a better fit to certain isotherms. Evidence of autocatalysis in the case of $[Fe(bipy)_3]Br_2 \cdot 5H_2O$, $[Ni(bipy)_3]Br_2 \cdot 5H_2O$ and $[Co(bipy)_3]Br_2 \cdot xH_2O$ was provided by the systematic negative deviation from the $\log[\alpha/(1-\alpha)] = kt + c$ plots for these compounds before $\alpha \sim 0.3$. In these systems the Prout and Tompkins equation held best in the range of $\alpha = 0.3$–0.82.

Apparatus. An Aminco automatic recording Thermograv balance was used for recording the thermograms and the isotherms. The temperature was controlled within a maximum variation of ±0.5° for the isothermal experiments. The balance employs a spring with a transducer assembly. The sample temperature was measured through an alumel–chromel thermocouple with its tip positioned at a distance of about 1.5 cm from the sample.* The sample holder constructed for this purpose was a Pyrex glass flat dish of 2.1 cm diameter.

A Gouy balance was utilized for measuring the magnetic moments of the compounds. The reflectance spectra were obtained on a Beckman DU spectrophotometer equipped with standard reflectance attachment and using powdered magnesium carbonate as standard.

Preparation of the compounds. The compounds were prepared either directly by methods given in the literature or by slight adaption of them whenever necessary. The analysis data are given in Table 2.

TABLE 2. ANALYSIS OF STARTING MATERIALS AND DECOMPOSITION PRODUCTS

	Calculated (%)					Observed (%)				
	C	H	N	Co	Br	C	H	N	Co	Br
$[Mn(bipy)_3]Br_2$	52.4	3.52	12.4			52.46	3.33	12.4		
$[Fe(bipy)_3]Br_2 \cdot 5H_2O$	46.6	4.4	10.82			46.8	4.55	11.08		
$Fe(bipy)_{1.5}Br_2$	40.04	2.67	9.34			39.3	2.89	9.01		
$Fe(bipy)Br_2$*	32.4	2.14	7.54			32.6	2.19	7.47		
$[Co(bipy)_3]Br_2 \cdot 3.5H_2O$	48.0	4.05	11.18	7.82	21.3	48.0	4.36	11.3	7.84	20.7
$[Co(bipy)_3]Br_2 \cdot 2.5H_2O$	49.2	3.96	11.4	8.13	21.8	49.42	3.77	11.5	7.98	22.5
$[Co(bipy)_3]Br_2 \cdot 5H_2O$	46.5	4.4	10.85			46.3	4.19	10.96		
$[Ni(bipy)_3]Br_2 \cdot 5H_2O$	46.5	4.38	10.8			46.75	4.50	11.03		
$Ni(bipy)_{1.5}Br_2$†	39.8	2.66	9.27		35.4	38.80	2.65	9.10		35.9
$Ni(bipy)_{1.5}Br_2$‡						40.16		9.44		35.8
$[Cu(bipy)_3]Br_2 \cdot H_2O$	50.6	3.66	11.8			50.3	3.58	12.06		
$Cu(bipy)_2Br_2$	44.9	2.98	10.46			43.96	3.22	10.57		
$Cu(bipy)Br_2$	31.6	2.11	7.29			31.6	2.15	7.56		
$[Zn(bipy)_3]Br_2 \cdot 4H_2O$	47.2	4.13	10.95			47.28	4.30	10.86		

* Obtained as a constant weight residual product between 215–225°C from thermogravimetric decomposition of $[Fe(bipy)_3]Br_2 \cdot 5H_2O$ (Fig. 1, Curve *B*).

† Obtained by the thermal dissociation of $[Ni(bipy)_3]Br_2 \cdot 5H_2O$.

‡ Obtained by direct synthesis as described in the text.

The compound $Mn(bipy)_3Br_2$ was prepared by the method of BURSTALL and NYHOLM(16). The method of BURSTALL and NYHOLM was also used for the preparation of $[Fe(bipy)_3]Br_2 \cdot 5H_2O$. The only difference being that the complex was precipitated from solution by addition of an excess of sodium bromide and the desired product was then dried over concentrated sulphuric acid. Essentially the same procedure was used for the synthesis of $[Ni(bipy)_3]Br_2 \cdot 5H_2O$.

The compound $[Co(bipy)_3]Br_2 \cdot xH_2O$ was prepared by a method similar to that reported by BURSTALL and NYHOLM for the corresponding perchlorate salt. The solutions were well purged with

---

* It must be recognized that a source of error in such instruments is that the actual sample temperature may be different from the recorded temperature due to the heat of reaction of the system.

(16) F. H. BURSTALL and R. S. NYHOLM, *J. Chem. Soc.* 3570 (1952).

TABLE 3 — ENERGY OF ACTIVATION AND RATE CONSTANTS FOR THE FIRST STEP THERMAL DISSOCIATIONS OF THE SOLIDS $M(bipy)_3Br_2$

Compound	Temperature (°C)	$k(\text{min}^{-1})$	Energy of activation (kcal mole^{-1})
$[Fe(bipy)_3]Br_2$	168.0	0.123	
	170.0	0.223	
	171.0	0.271	
	172.0	0.276	76.5
	174.5	0.453	
	176.5	0.736	
	177.0	0.818	
$[Ni(bipy)_3]Br_2$	189.5	0.0965	
	193.5	0.193	
	196.5	0.308	56.6
	199.5	0.446	
	203.5	0.608	
$[Cu(bipy)_3]Br_2$ Sample No. 1	44.5	0.110	
	45.7	0.132	
	48.75	0.177	24.2
	50.50	0.237	
	53.5	0.320	
	53.8	0.308	
	55.1	0.430	
$[Cu(bipy)_3]Br_2$ Sample No. 2	45.5	0.155	
	46.3	0.175	
	49.3	0.234	24.6
	52.25	0.326	
	53.25	0.413	

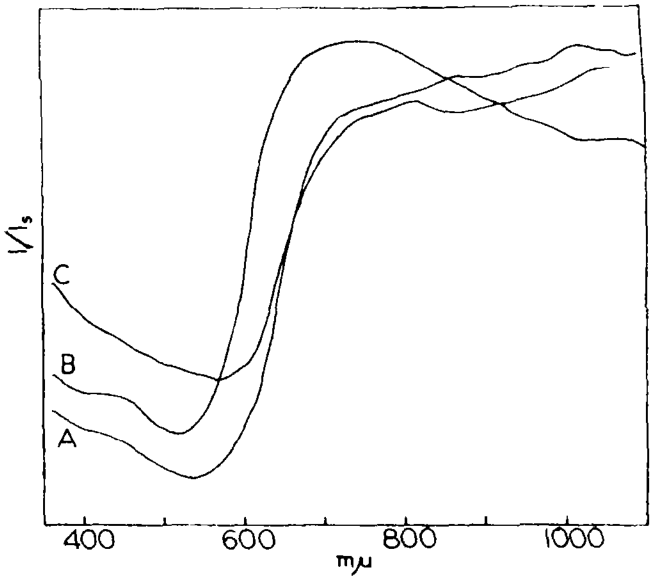


FIG. 4 – Reflectance spectra of

A $[Fe(bipy)_3][FeBr_4]$ I/I_s Intensity of the sample
B $Fe(bipy)Br_2$ and Intensity of the $MgCO_3$ standard
C $[Fe(bipy)_3]Br_2$

nitrogen to expel the dissolved oxygen and excess sodium bromide was added to precipitate [$Co(bipy)_3$]$Br_2 \cdot xH_2O$. The compound was dried under vacuum overnight, but variable hydrate compositions were obtained for different preparations.

The procedure of JAEGER and VAN DIJK(17) for the synthesis of [$Cu(bipy)_3$]$SO_4 \cdot 7H_2O$ was used to prepare the bromide salt. Excess sodium bromide was added to the reaction mixture and the resulting bromide was recrystallized from water and dried over concentrated sulphuric acid to yield [$Cu(bipy)_3$]$Br_2 \cdot H_2O$. This same procedure was used for the synthesis of $Zn(bipy)_3Br_2 \cdot 4H_2O$.

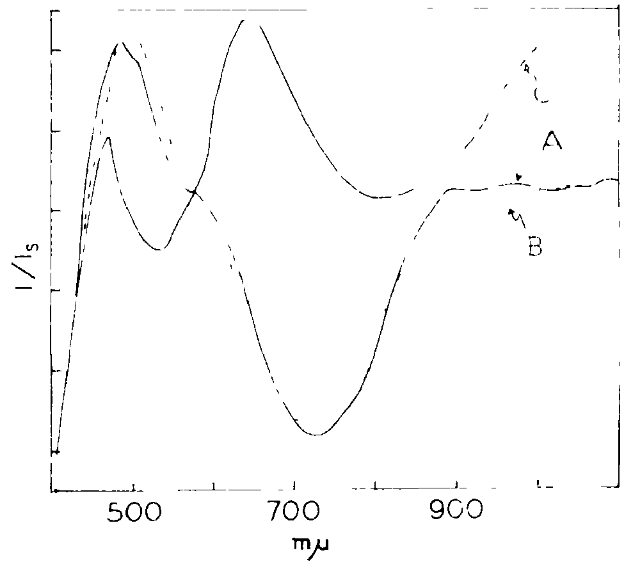


FIG. 5. Reflectance spectra of
A. [$Ni(bipy)_3$][$NiBr_4$]: Thermal decomposition product of [$Ni(bipy)_3$]$Br_2 \cdot 5H_2O$.
B. [$Ni(bipy)_3$][$NiBr_4$]: Synthetic product (see text).
C. [$Ni(bipy)_3$]$Br_2 \cdot 5H_2O$.

In the case of the nickel(II) and cobalt(II) compounds an attempt was made to obtain the anhydrous salt by carrying out the synthesis in absolute ethanol. Thus 1.114 g of anhydrous $NiBr_2$ was added to 2.34 g of bipyridine dissolved in 80 ml of ethanol. The mixture was refluxed for 30 min and then the solution was concentrated to ca. 30 ml. Addition of excess ether resulted in the precipitation of [$Ni(bipy)_3$]Br_2. The compound readily absorbs about 2.5 equivalents of water from the atmosphere.

A solution of 0.32 g of anhydrous $CoCl_2$ in 15 ml nitrogen purged absolute ethanol was added to 0.55 g of bipyridine dissolved in 10 ml ethanol. Nitrogen was passed through the solution for 10 min at room temperature and then an excess of ether was added. A fine precipitate of [$Co(bipy)_3$]Br_2 was obtained which was dried under vacuum overnight. Like the nickel complex [$Co(bipy)_3$]Br_2 also readily absorbs about 2.5 equivalents of water from atmosphere.

Acknowledgements. This research was supported by the Advanced Research Projects Agency of the Department of Defense through the Northwestern University Materials Research Centre. The authors thank Professor R. G. PEARSON for helpful discussions.

(17) F. M. JAEGER and J. A. VAN DIJK, *Z. Anorg. Chem.* **227**, 273 (1936).

J Inorg Nucl Chem 1963 Vol 25 pp 45 to 55 Pergamon Press Ltd Printed in Northern Ireland

THE PYROLYSIS OF DIVALENT METAL 8-QUINOLINOL CHELATES

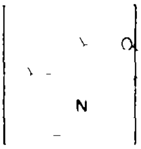
R G CHARLES, A PERROTTO and M A DOLAN
Westinghouse Research Laboratories Churchill Borough
Pittsburgh 35, Pennsylvania

(*Received* 20 *April* 1962, *in revised form* 14 *June* 1962)

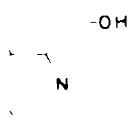
Abstract The pyrolytic behaviour, in an inert atmosphere, of a series of divalent metal chelates derived from 8-quinolinol has been studied The order of decreasing heat stability of the compounds is Ca Mg Sr $\sim$ Cd $\sim$ Mn Ba Co Ni Zn Pb Cu Principal products of decomposition include H_2, 8-quinolinol, the free metal or the metal oxide, and carbonaceous materials in which a portion of the metal chelate ring systems is retained For those 8-quinolinolates which give the free metals, the relative heat stabilities appear to be determined by the ease with which the divalent cations are reduced to the metallic form

DURING the past several years there has been considerable interest in the preparation of metal chelate polymers as possible heat stable materials[1] Surprisingly little is known, however, concerning the inherent heat stabilities of metal chelate ring systems which might be incorporated into such polymers Little is known also of the nature of the decomposition products formed on pyrolysis or of the effect upon heat stability of such parameters as the nature of the metal The present paper represents part of a continuing programme to obtain fundamental information in these areas through a study of model compounds

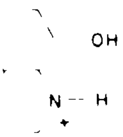
Previous work[2,3] in this laboratory has established that certain of the divalent metal 8-quinolinolates (oxinates, I) especially those derived from the alkaline earth metals, possess relatively high heat stabilities We have now studied in greater detail the pyrolytic behaviour of the oxinates derived from most of the remaining divalent metals which form well characterized chelates[4] with 8-quinolinol (8-hydroxyquinoline oxine, II) The metals employed are Cu, Ni Co Mn, Zn Cd and Pb



I



II



III

---

* Presented at the 141st National Meeting of the American Chemical Society Washington D C March 1962

[1] For recent reviews concerning coordination polymers see C W KENNEY *Chem and Industr* (London) 880 (1960) D B SOWERBY and L F AUDRIETH *J Chem Educ* 37, 134 (1960)

[2] R G CHARLES and A LANGER, *J Phys Chem* **63**, 603 (1959)

[3] R G CHARLES, *J Inorg Nucl Chem* **20**, 211 (1961)

[4] R G W HOLLINGSHEAD, *Oxine and Its Derivatives*, Vols I and II Butterworth Publications London (1954)

RESULTS AND DISCUSSION

1. *Preparation of compounds*

The divalent metal oximates are routinely prepared as precipitates from aqueous solution during the gravimetric determination of the respective metals.(4) There are few descriptions in the literature, however, of the preparation of these compounds in quantity. When prepared by the method given in the Experimental Section, and dried at room temperature, all the compounds except the Pb and Cu oximates were obtained as the dihydrates. The latter two compounds were anhydrous. This is shown by the thermogravimetric curves of Fig. 2, where no weight loss occurs below 300°C, and also by the metal analyses in Table 1. All of these oximates, including the Pb and Cu chelates have been reported to form dihydrates.(5,6) Apparently the hydrates of the latter two chelates are not stable, however, at room temperature and normal (30-50 per cent) humidity.

TABLE 1.—COMPOSITION OF DIVALENT METAL 8-QUINOLINOL CHELATES DRIED AT ROOM TEMPERATURE

	Metal (%)		H_2O (%)	
	Calcd	Found	Calcd	Found*
$Cu(C_9H_6NO)_2$	18.07	18.1	0	0.0
$Ni(C_9H_6NO)_2 \cdot 2H_2O$	15.33	15.2	9.41	9.9†
$Co(C_9H_6NO)_2 \cdot 2H_2O$	15.37	15.3	9.40	9.7
$Mn(C_9H_6NO)_2 \cdot 2H_2O$	14.48	14.1	9.50	9.2
$Zn(C_9H_6NO)_2 \cdot 2H_2O$	16.78	16.6	9.25	8.9
$Cd(C_9H_6NO)_2 \cdot 2H_2O$	25.70	26.1	8.25	8.1
$Pb(C_9H_6NO)_2$	41.80	41.2	0	0.0

* Initial weight losses from thermogravimetric runs in argon.

† Weight loss to 180°C. A small additional weight loss, apparently due to liberation of oxine through interaction of water with the oximate, occurs between 180° and 220°C.

2. *Comparative heat stabilities*

The least ambiguous method which was found for comparing the heat stabilities of the oximates is based on changes in ultra-violet absorption spectra as pyrolysis progresses. Each of a series of weighed samples of the dehydrated oximate is sealed in an evacuated glass tube and heated at constant temperature for a constant period of time. The tube is cooled, broken open, and the contents extracted with aqueous HCl. After quantitative dilution the optical absorbance at 252 mμ is measured. The absorbance (due to the quantitative formation of the ion III from remaining oximate(3)) and the pyrolysis temperature define one point in Fig. 1. The entire procedure is repeated to obtain other points.

This method is quite tedious but it circumvents certain difficulties inherent in the other two procedures described below. For the latter two methods (but not for the method just described) volatilization of unchanged starting material or the exclusive formation of nonvolatile pyrolysis products can create serious problems of interpretation.

---

(5) M. BORREL and R. PARIS, *Analyt. Chim. Acta* **4**, 267 (1950).

(6) L. L. MERRITT, *Analyt. Chem.* **25**, 718 (1953).

Any departure from the initial horizontal portions of the curves in Fig 1 must be due to pyrolysis. Completion of pyrolysis is accompanied, for most of the compounds, by a drop in absorbance to zero The curves for Cu and Pb oximates differ from the others in that the absorbance does not fall sharply to zero As shown below this is due, in these instances, to the formation of oxine as a major pyrolysis product Oxine dissolves in acid to give the same ion III as does unpyrolysed metal oximate

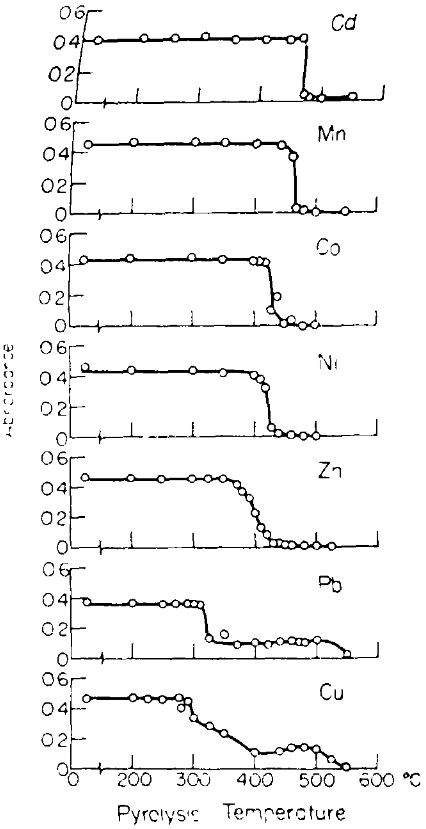


FIG. 1 Variation of absorbance with pyrolysis temperature for divalent metal 8-quinolinol chelates Each point represents a separately heated sample dissolved in 0 1M aqueous HCl Heating time was 4 hr The points given are for the anhydrous chelates except for those at 25°C

The temperature at which pyrolysis first becomes detectible under the conditions used varies over a wide range from about 275 C for the copper chelate to approximately 460°C for cadmium oximate The relative heat stabilities of the metal oximates can be determined by a comparison of the position, along the temperature axis, of the sharply descending portions of the curves in Fig 1 The order of decreasing heat stability (which includes results obtained previously for the alkaline earth oximates) is Ca Mg Sr ~ Cd ~ Mn Ba Co Ni Zn ~ Pb - Cu Although there are appreciable differences in heat stability between widely separated members of this series there is little difference between adjacent members

The position of the oxine, itself, in this sequence is not entirely clear Previous work[3] has shown that oxine begins to decompose at temperatures below those necessary to decompose the Co, Ni and Zn oxinates It is not completely decomposed, however, at 460 C where these three chelates are completely pyrolysed It appears that oxine belongs between Ba and Pb

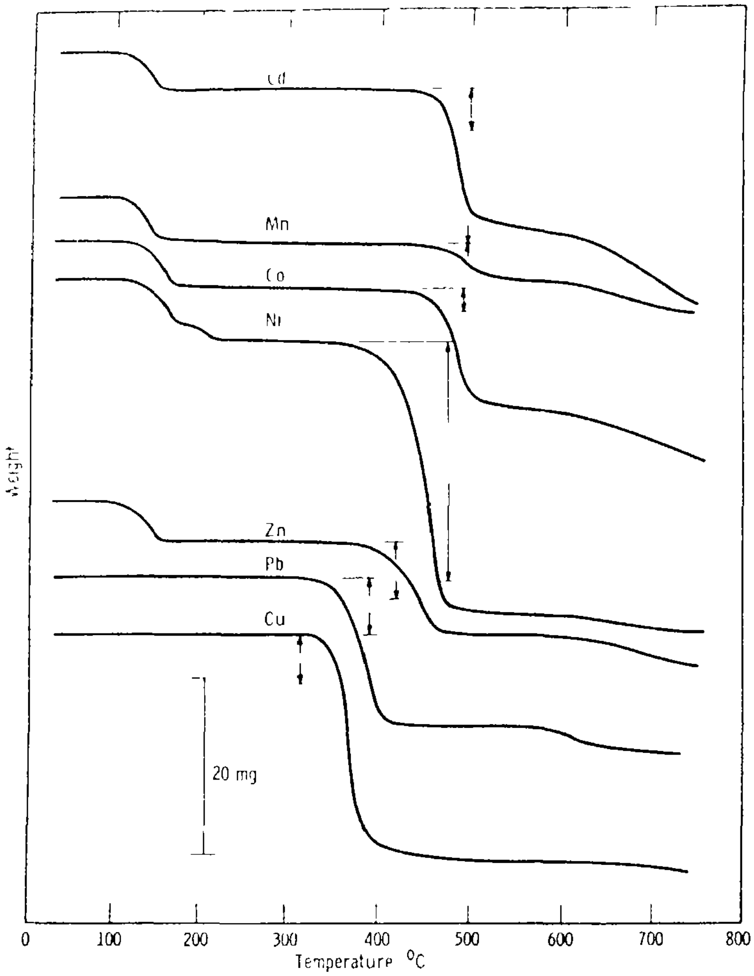


FIG 2 Weight loss temperature curves for hydrated divalent metal 8-quinolinol chelates heated in argon at atmospheric pressure Fifty milligrams samples were used Arrows show weight losses due to evaporation of unchanged chelate

To supplement the sealed tube measurements, we have studied the thermogravimetric (TGA) behaviour of the oxinate hydrates in a slow stream of argon at atmospheric pressure The TGA curves obtained are given in Fig 2 Weight losses to about 200°C are due to loss of water of hydration and have been used to calculate the numerical values for water content given in Table 1 Weight losses beyond 200°C must be due to evaporation of volatile pyrolysis products and/or evaporation of unchanged chelate For all the compounds, except Mn oxinate, condensation of sublimed chelate outside the furnace could be observed visually in the temperature range, above 200°C, corresponding to weight loss in Fig 2 The amount of oxinate sublimed was calculated from metal analysis of the residue (to 500°C) utilizing the reasonable assumption that the oxinate was the only volatile metal-containing species * The quantities so calculated are indicated in Fig 2 Sublimed oxinate accounts for most of the observed weight loss above 200°C for the Ni chelate and for appreciable fractions of the weight losses for other chelates, with the exception of that for Mn oxinate Remaining weight losses above 200°C must be due to decomposition

Judging from the appearance of the curves there must be considerable overlap in the temperature regions of sublimation and decomposition For most of the curves in Fig 2 sublimation obscures the temperature at which pyrolysis first becomes significant Inspection of the higher temperature portions of the curves where decomposition predominates, however, leads to the same order of decreasing heat stability deduced from Fig 1, and given above The temperature regions over which decomposition occurs on the thermobalance appear to be shifted to slightly higher temperatures with respect to the corresponding regions in Fig 1 This is to be expected in view of the more prolonged heating involved in the sealed tube experiments

It should be noted that the curves of Fig 2 are quite different from those obtained previously in high vacuum (2) Under the latter conditions most of the oxinates volatilize completely at temperatures below those necessary for pyrolysis The curves of Fig 2 also differ significantly from those obtained by other workers(5,7) in air In an atmosphere of air oxidation by oxygen and hydrolysis by water vapour undoubtedly play important roles and the results are not directly comparable with those obtained here

A third method of comparing heat stabilities involved following pressure changes in a closed glass system containing the metal oxinate and argon (near atmospheric pressure) as that portion of the apparatus containing the oxinate was heated The remainder of the apparatus was kept at room temperature By analogy with thermogravimetric analysis (TGA) we have termed the present procedure thermomanometric analysis (TMA) TMA resembles TGA in that it is responsive to the formation of volatile products Unlike TGA however, TMA is sensitive only to permanent gases or to compounds having high vapour-pressures at room temperature Less volatile materials condense on the cooler portions of the apparatus and do not contribute significantly to the total pressure TMA is responsive to products on a molar rather than on a weight, basis and hence is more sensitive to the formation of products of low molecular weight such as H_2, than is TGA

In Fig 3, TMA curves are given for each of the anhydrous metal oxinates These curves have been calculated from the raw data by deducting the increase in pressure due to heating the argon Because of the relatively static gas atmosphere and the difference in geometry of the apparatus, sublimation of unchanged oxinate was much less serious here than in the TGA experiments and could be neglected

Evolution of gas (Fig 3) begins at temperatures a little above the corresponding temperatures where decomposition first becomes detectible in Fig 1 Gases continue to be evolved up to the highest temperatures employed although there is some tendency for the curves to level off after all the starting chelate has undergone pyrolysis It is apparent that the gases produced at the highest temperatures come from further decomposition of initially produced pyrolysis products The Pb and Cu oxinates were

---

* For Cd oxinate this appeared to be true of the thermogravimetric run Prolonged isothermal heating at 500 C, however, resulted in measurable volatilization of Cd metal

(7) C DUVAL, *Inorganic Thermogravimetric Analysis* Elsevier New York (1953)

observed to give off less gas than the other chelates The Pb chelate repeatedly gave erratic behaviour in the temperature range 450–600 °C, although the general shape of the curve was not changed We have no explanation for this behaviour The order

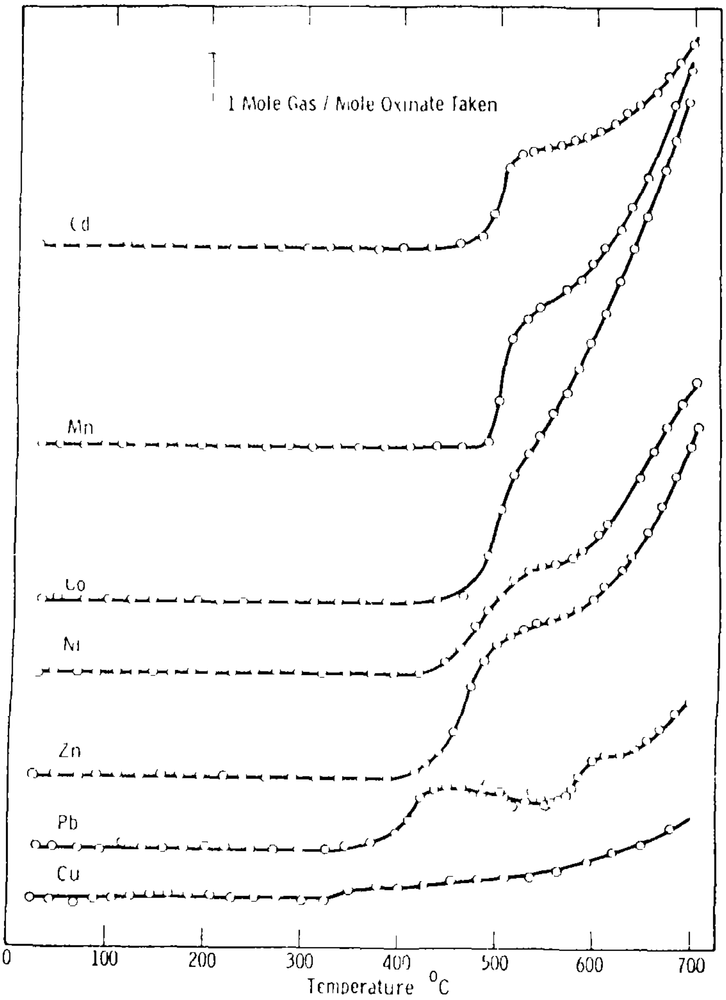


FIG 3—Gas evolution from metal 8-quinolinol chelates upon heating in argon at 2 9 C/min The horizontal portion of each curve corresponds to zero gas evolution

of decreasing heat stability based on the temperature at which gaseous decomposition products are first detected in Fig 3 is the same as that deduced from Fig 1

3 *Pyrolysis products*

The products of decomposition can conveniently be classed into two groups (a) those volatile at the pyrolysis temperature and (b) non-volatile materials which comprise the residues

The identities of the gaseous components of group (a) were established by separate experiments in which the anhydrous oxinates were heated at constant temperature under argon in sealed glass tubes After cooling to room temperature the gas phase was analysed with a mass spectrometer. The results are given in Table 2. The principal gaseous product in each case was H_2. At 700°C this was accompanied by significant amounts of CH_4, CO and CO_2. Nitrogen was also given off by the Ni, Co, and Zn oximates at the higher temperatures.

The only other volatile product identified was oxine. This was identified in each instance by its ultra-violet absorption spectrum and by the melting points of the white needle-like crystals which formed on the cooler portions of the tubes during pyrolysis. The quantities formed (Table 2) were determined by dissolving the sublimed material from the gas determinations above in aqueous HCl and determining the optical absorbance at 252 mμ. The results are listed in Table 2. As evident from Table 2 oxine is produced principally at the lower pyrolysis temperatures where the chelate rather than its initially formed pyrolysis products is decomposing.

TABLE 2.—VOLATILE DECOMPOSITION PRODUCTS FROM ANHYDROUS METAL 8-QUINOLINOL CHELATES HEATED 4 HR IN ARGON

		Mole ratios Product/oximate taken					Fractional weight loss	
Metal	Temp (°C)	H_2	CH_4	CO	CO_2	Oxine	Obs*	Sum of products
Cu	500	0.11	0	0.04	0.03	1.14	0.50	0.42
	700	0.55	0.03	0.24	0.12	1.23	—	—
Ni	500	0.47	0.02	0.12	0.05	0.54	0.24	0.27
	700†	2.17	0.30	0.73	0.17	0.35		
Co	500	1.07	0.07	0.25	0.25	0.22	0.27	0.17
	700‡	4.26	0.44	0.86	0.27	0.14	—	—
Mn	500	1.03	0.02	0.02	0.01	0.05	0.10	0.03
	700	2.67	0.39	0.80	0.02	0.04	—	
Zn	500	1.15	0.02	0.02	0.01	0.12	0.07	0.07
	700**	1.30	0.38	0.82	0.07	0.14		—
Cd	500	0.52	0.03	0.03	0.03	0.62	††	0.26
	700	1.39	0.17	0.25	0.24	0.69	—	—
Pb	500	0.14	0	0.07	0.02	0.96	0.25	0.29
	700	0.86	0.08	0.26	0.17	1.04	—	

* Calcd from metal content of residue.

† 0.43 mole ratio N_2.

‡ 0.74 mole ratio N_2.

** 0.14 mole ratio N_2.

†† Not calcd because of volatility of Cd metal.

The sum of the weights of the products listed is compared with the total weight loss due to decomposition in Table 2. The products listed account for most of the weight loss. In the case of cobalt oximate there is a significant difference between the observed weight loss and the sum of the products listed. This indicates that other unidentified, volatile products must be formed. Smaller amounts of such products may be formed also by the other chelates.

Elemental analyses of the nonvolatile residues remaining from pyrolysis at 500°C are given in Table 3 together with the species identified by X-ray diffraction powder patterns. The residues contain appreciable amounts of C, H, N and O in addition to metal.

The Cu, Ni, Co, Cd and Pb oxinates are seen to give the free metals as pyrolysis products while Mn and Zn oxinates give the oxides. The ferromagnetism of Ni and Co was used as a basis for determining the amounts of these metals in the pyrolysis residues. By magnetic susceptibility measurements 54 per cent of total Ni content and 41 per cent of the Co were found to be present as the free metals at 500°C.

TABLE 3. COMPOSITION OF ANHYDROUS NONVOLATILE RESIDUES FROM THE PYROLYSIS OF ANHYDROUS 8-QUINOLINOL CHELATES (4 HR AT 500°C IN ARGON)

Metal	Elemental analyses (wt %)					Species identified
	M	C	H	N	O*	
Cu	36.8	44.0	1.54	5.55	12	Cu
Ni	22.5	58.0	2.66	8.05	9	Ni
Co	23.4	59.8	2.27	7.31	7	Co
Mn	17.6	58.8	2.74	5.22	16	MnO
Zn	19.8	59.0	2.72	5.48	13	ZnO
Cd	29.7	52.1	2.57	6.26	9	Cd
Pb	55.9	30.6	1.36	3.82	8	Pb†

* By difference.
† Also weak lines not due to PbO.

TABLE 4. RELATIONSHIP BETWEEN STANDARD METAL OXIDATION POTENTIALS AND RESISTANCE OF THE 8-QUINOLINOL CHELATES TO PYROLYSIS

Metal	Oxinate decomp temp (°C)	$-E^0$
Cu	275	0.337
Pb	310	0.126
Ni	400	0.250
Co	420	0.277
Cd	460	0.403

For those oxinates which give free metal on pyrolysis a correlation was observed between heat stability and the ease with which the divalent metal ion can be reduced to the metallic form. In Table 4 the standard oxidation potentials(8) of the metals are compared with the temperatures (Fig. 1) at which decomposition of the oxinates first becomes detectible. A definite parallelism is seen to exist with the oxinates of the most easily reduced cations the most susceptible to pyrolysis. Mn and Zn oxinates, which give the oxides, are less heat stable than would be predicted by the observed relationship.

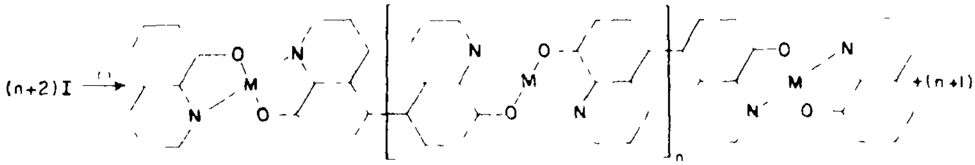
It is interesting that the oxinates which are most resistant to heat are not the ones which are most resistant to dissociation (to ions) in aqueous solution. On the contrary a rough *inverse* relationship seems to exist between heat stability and the reported solution stability constants[9,10] for the metal oxinates.

---

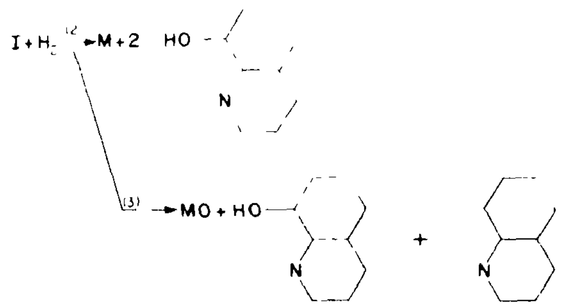
(8) W. M. LATIMER, *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions*, (2nd Ed.) Prentice-Hall, New York (1952).

4 *Pyrolysis mechanism*

Most of the data obtained at the lower pyrolysis temperatures can be accounted for satisfactorily by the Equations (1)–(3) below.



IV



The first step (1) in the proposed mechanism involves intermolecular dehydrogenation between metal oxinate molecules to give polymeric structures in which the metal chelate ring systems are retained. IV is one of a number of possible structures. The hydrogen released may be evolved as H_2 or may react with remaining I by the paths (2) or (3) to give the products indicated. The facility with which I can act as a hydrogen acceptor may determine the relative heat stabilities of those oxinates which react by path (2).

Equations (1) and (2) require that the molar sum of (H_2 + ½oxine) equal the number of moles of oxinate taken, when n is large. The experimental values at 500° C (Table 2) for the ratio [(H_2 + ½oxine)/oxinate] lie in the range 0.62–1.18. At higher temperatures this ratio becomes much larger than 1 due to increased evolution of H_2. This additional evolution of H_2 must involve inter- and intra-molecular dehydrogenation of initially formed products, such as IV. That the dehydrogenation at the higher temperatures is accompanied by partial disruption of the metal chelate ring systems is shown by the formation of the other gaseous products listed in Table 2. At 700° C even the quinoline nucleus is disrupted to some extent as evidenced by the evolution of N_2 from the Ni-, Co-, and Zn-containing materials.

Equations (1) to (3) can be considered only an approximation to the true state of affairs even at the lower pyrolysis temperatures. In the two instances where a direct measure was obtained of the amount of metal (Ni and Co) produced at 500° C the quantities are greater than can be accounted for by Equation (2). In order to fit these

---

[9] R Nasanen, *Suom Kem* B **2**, 11 (1953)

[10] W D Johnston and H Freiser, *Analyt Chim Acta* **11**, 201 (1954)

data into the above scheme, it is necessary to postulate additional oxidation reduction reactions involving IV which do not evolve H_2 or oxine.

EXPERIMENTAL

Preparation of compounds

Seven and five tenths grammes (0.052 mole) of 8-quinolinol was dissolved in 200 ml methanol. To this solution was added with stirring 0.025 mole of the divalent metal acetate dissolved in 500 ml of water. This was followed by a solution of 0.075 moles* of sodium acetate in 100 ml water. The mixture was heated nearly to boiling, cooled to room temperature, and the precipitate was filtered off on a Buchner funnel. The compound was washed repeatedly with hot water. It was then dried in the air at room temperature for about a week and finally stored in a tightly capped jar to prevent further changes in hydration. Yields were practically quantitative. Analyses are given in Table 1.

Sealed tube experiments

Each of a series of 100 mg samples of the air-dried oxinates was weighed into a Pyrex glass tube of about 4 ml capacity. The open tubes were then heated overnight at 150°C in a vacuum oven. Previous work[2] had established that all the compounds dehydrate completely under these conditions. The tubes were cooled in a desiccator, evacuated to a pressure of about 3μ, and sealed with a torch. Each tube was then heated for 4 hr in a constant temperature furnace with the entire tube within the hot zone.

Each cooled tube was wrapped in sheet polyethylene and broken open with a hammer. The unreacted oxinate was extracted by stirring with 20 ml of 1M aqueous HCl. In some instances gentle heating was necessary. The extract was filtered into a 500 ml volumetric flask. The beaker, polyethylene, and filter were washed with 0.1M HCl which was added to the filtrate. The combined filtrate was made up to 500 ml with 0.1M HCl. An aliquot of this solution was further diluted 1 to 100 with 0.1M HCl. The absorbance (optical density) of the diluted solution at 252 mμ was measured with a Cary model 14 spectrophotometer using 1 cm quartz cells. The measured absorbance and pyrolysis temperature for each tube was used to define one point on the plots given in Fig. 1. The points at 25°C in Fig. 1 were obtained as above but by using the products directly which had not been dehydrated and which had not been sealed into glass tubes or heated.

Thermogravimetric analysis

The balance previously described[2] was employed. For the present experiments, however, the balance was operated at atmospheric pressure. A slow stream (50 ml/min) of high purity argon flowed over the sample during the run. Air was rigorously excluded. The sample was contained in a shallow platinum cup. Temperature was increased at a linear rate of 2.1°C/min. Temperature weight plots were obtained directly with a Moseley X-Y recorder.

Thermomanometric analysis

The apparatus consisted of a vertical quartz furnace tube about 15 mm diameter and 100 ml capacity, sealed at the lower end. The bottom third of the tube was supported within a Hoskins tube furnace. The upper end of the tube (at room temperature) communicated by means of an O-ring joint and stopcock arrangement to a modified Warburg open-end manometer. The latter employed mercury as the manometric fluid.

The sample was contained in a small quartz cup which rested on the bottom of the furnace tube in close proximity to a thermocouple well indented through the wall of the furnace tube. Temperature was measured by means of a chromel-alumel thermocouple. The furnace temperature was raised linearly with time by means of a synchronous motor-driven Variac. The rate of temperature increase was 2.9°C/min.

For a run, 3×10^{-4} mole of the chelate was weighed into the sample cup and dehydrated in the vacuum oven for two or more hours at 150°C. The apparatus was assembled and alternately evacuated and refilled with argon several times to displace the air. Finally the pressure was brought to about 525 mm Hg and the apparatus sealed off by means of a stopcock. Heating was then begun. Pressure, temperature and barometer readings were taken at intervals. The total pressure increase during a typical run (Mn oxinate) was 360 mm Hg of which about 200 mm Hg was due to the formation of decomposition products.

A series of calibration runs were carried out in which known quantities of argon, alone, were heated as above From the pressure–temperature relationships obtained, linear plots could be constructed relating the number of moles of gas present in the system to observed pressure readings at any furnace temperature A family of such plots was used to construct the curves of Fig 3 from the pressure readings obtained during runs with the oxinates Implicit in this treatment is the assumption that a mole of gaseous decomposition product will make the same contribution to the total pressure as a mole of argon This is only approximately true but sufficiently accurate results are obtained for the present purposes where intercomparisons between related materials are the prime considerations Results obtained are consistent with those from the different procedure, utilizing a mass spectrometer, which is described below

---

* For the preparation of the Cu, Ni, and Pb chelates 0.05 mole were used.

Mass spectrometer analysis

One hundred mg samples of the air-dried chelates were dehydrated in the vacuum oven Each sample was sealed in a cylindrical Vycor glass tube equipped with a stopcock arrangement under a measured pressure of about 525 mm Hg of argon The tubes were heated 4 hr at constant temperature using a thermostatically controlled tube furnace Volatile decomposition products were free to condense on cool portions of the tube outside the furnace After cooling for several hours, each tube was attached to the mass spectrometer (Consolidated No 21-103) and a gas sample taken The number of moles of each gaseous product could be calculated from the known amount of argon taken and the mole ratio of product to argon, obtained from the mass spectrometer data

The sublimed material from each run was dissolved in 1M HCl The resulting extract was analysed separately for metal and for oxine (spectrophotometrically as described above) A negligible amount of metal was found in the sublimate except for the Cd oxinate run where a significant amount of Cd metal volatilized from the heated zone

Studies involving nonvolatile residues

Samples of the nonvolatile mixtures resulting from pyrolysis were obtained by heating at constant temperature 1 g portions of the dehydrated oxinates contained in shallow quartz boats, in a slow stream of argon A thermostatically controlled tube furnace was employed The dark colored residues were cooled in argon and ground to a powder The powdered materials all had a tendency to absorb several per cent of their weight of water when exposed to air of normal humidity In all cases this could be removed by heating to 100°C All analysis for these materials refer to the dry basis

Carbon hydrogen, and nitrogen elemental analyses were performed by the Galbraith Laboratories Knoxville, Tennessee Metal analyses were carried out using accepted macro procedures Magnetic susceptibility measurements were carried out on the dry residues from the Co and Ni oxinates The Faraday method(11) was used Metal contents were calculated using the saturation magnetic moment values σ_s 54 4 e m u/g and σ 161 e m u/g for Ni and Co metals respectively (12) The susceptibility extrapolated to infinite magnetic field was used for the Co residue calculations

Acknowledgement—The writers are grateful to Dr W M Hickam for the mass spectrometer results to Dr D I Cox for the magnetic susceptibility measurements and to Miss B Kagle for the X-ray diffraction determinations

(11) P W Selwood, *Magnetochemistry* (2nd Ed) p 11 Interscience New York (1956)

(12) R M Bozorth, *Ferromagnetism* Van Nostrand, New York (1951)

J. Inorg. Nucl. Chem. 1963 Vol. 25 pp. 57 to 66. Pergamon Press Ltd. Printed in Northern Ireland

THE CHEMISTRY OF PROTACTINIUM—I

THE NATURE OF SPECIES IN HCl SOLUTIONS BY SOLVENT EXTRACTION AND PAPER ELECTROPHORESIS

J. SHANKAR, K. S. VENKATESWARLU and C. GOPINATHAN
Chemistry Division, Atomic Energy Establishment Trombay, Bombay, India

(*Received* 25 *April* 1962, *in revised form* 19 *June* 1962)

Abstract In this paper, experiments on the extraction of ^{233}Pa into tri-n-butyl phosphate from hydrochloric acid solutions are described. The effect of fluoride, phosphate, citric, lactic and tartaric acids on the distribution coefficient was studied. Ethyl acetoacetate was found to be a good extracting agent.

A semi-closed type apparatus has been designed for use in electro-phoresis studies of ^{233}Pa in HCl solutions. From the variation of the anion/cation ratio with the concentration of HCl the nature of the cation to anion conversions could be inferred. The mobility of ^{233}Pa is greatly enhanced by the presence of traces of fluoride ion, and the histograms clearly indicate the presence of cationic species.

EARLIER observations e.g.$^{(1-4)}$ on the extraction of protactinium into organic solvents such as di-isopropyl carbinol, nitrobenzene etc., have indicated that the distribution coefficients are affected by acidity and depend upon the complexing agents (e.g. oxalate) present in the aqueous solution. On the basis of their observations, CASEY and MADDOCK$^{(2)}$ have postulated a dynamic equilibrium involving a number of hydroxylated chloride species of Pa(V) in aqueous HCl solutions.

Very little work appears to have been carried out on the paper electrophoresis of protactinium solutions. This may be due to the difficulty in working with high acid concentrations requiring high currents.

JAKOVAC and LEDERER$^{(5)}$ studied the paper electrophoresis of protactinium in 1 N KOH while VERNOIS$^{(6)}$ reported the use of this technique in HCl(0.6 N)-HF(2 N) medium to effect the separation of ^{233}Pa from a number of other elements.

The present paper gives the results of a study of the extraction of ^{233}Pa from HCl solutions into tri-n-butyl phosphate and the effects of the fluoride, phosphate, citrate, tartarate and lactate ions on the distribution coefficients. The migration of protactinium using the paper electrophoresis technique was investigated to get a further insight into the nature of the species present in aqueous HCl solutions used for extraction.

EXPERIMENTAL

1-1 *Preparation of protactinium*-233

This was prepared by irradiation of very pure thorium nitrate in the Apsara reactor and the ^{233}Pa separated by the ion exchange method of KRAUS and MOORE.$^{(7)}$ The purity of ^{233}Pa was checked by measurements of its half-life, β-absorption and γ-spectrum. All the observations agreed very closely

---

(1) A. G. GOBLE and A. G. MADDOCK, *J. Inorg. Nucl. Chem.*, **7**, 94 (1958).

(2) A. T. CASEY and A. G. MADDOCK, *J. Inorg. Nucl. Chem.* **10**, 289 (1959).

(3) D. F. PEPPARD, G. W. MASON and M. V. GERGEL, *J. Inorg. Nucl. Chem.* **3**, 370 (1956).

(4) J. J. KATZ and G. T. SEABORG, *The Chemistry of Actinide Elements* p. 67, 93. Methuen, London (1958).

(5) Z. JAKOVAC and M. LEDERER, *J. Chromatography* **1**, 289 (1958).

(6) J. VERNOIS, *J. Chromatography* **2**, 155 (1959).

(7) K. A. KRAUS and G. E. MOORE, *J. Amer. Chem. Soc.* **72**, 4293 (1950).

with those reported earlier[8] The acidity of the stock solution stored in a polythene container, was maintained at 6 M HCl

1-2 *Solvent extraction procedure and measurement*

Tri-n-butyl phosphate used in these experiments was Eastman white label quality This was further purified by washing four times with 0.1 M sodium hydroxide and then an equal number of times with distilled water Ethyl acetoacetate was purified by distillation All other reagents used were of B D H AnalaR or E Merck G R quality

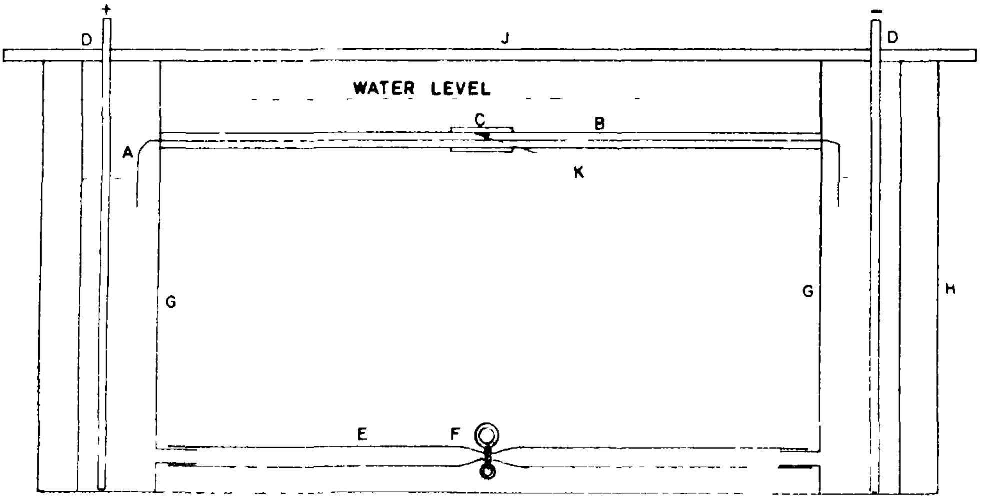
The solvent extractions were carried out in 10 ml polythene tubes with pushfit stoppers The adsorption of ^{233}Pa on these polythene tubes was found to be negligible The organic solvent (3 ml of undiluted TBP or 5 and 25% TBP in benzene) was pre-equilibrated with an equal volume of the aqueous phase containing ^{233}Pa at a known acid concentration The two phases were separated by centrifuging the container Two ml of this organic phase was taken in another polythene tube and was equilibrated with an aqueous phase of the same acidity as used before, but containing no protactinium This tube was mechanically shaken for 15 min and the two phases were again separated by centrifuging them This procedure eliminated the inaccuracies due to the presence of any inextractable species of ^{233}Pa It also took care of any extraction of hydrochloric acid by the solvents, and the ionic strength remained constant during the experiment as the partition of HCl is very small Aliquots of both the organic and aqueous phases were measured in a well type NaI (Tl) scintillation counting assembly using a single channel pulse height analyser All the measurements were made with a narrow channel width (0.5 V) at the position of 0.31 MeV peak of ^{233}Pa From the data, the distribution coefficient

$$K_d \quad ({}^{233}\mathrm{Pa})_{org}/({}^{233}\mathrm{Pa})_{aq} \qquad \text{was calculated}$$

The over all reproducibility was 1 per cent

1-3 *Paper electrophoresis procedure*

In a strong HCl medium the conductivity was very high and involved difficulties in operation so that the sandwich type of apparatus[9] could not be used, even slight non-uniformities in pressure leading to the disintegration of the paper This necessitated the development of a semi-closed unit with minimum evaporation losses The apparatus shown in Fig 1 was entirely made from Perspex



A PAPER STRIP B PERSPEX TUBE C PVC TUBE COVERING HOLE IN CENTRE
D GRAPHITE ELECTRODES E PVC TUBE FOR EQUALISATION OF LIQUID LEVELS
F PINCH COCK G ELECTRODE COMPARTMENTS H TANK CONTAINING COOLANT-WATER J LID K HOLE

FIG 1 —Sketch of the electrophoresis apparatus

---

(8) D STROMINGER J M HOLLANDER and G T SEABORG, *Rev Mod Phys* **30**, 814 (1958)

(9) M LEDERER, *An Introduction to Paper Electrophoresis and Related Methods*, p 41 43 Elsevier Publishing Company (1957)

The filter paper strip, A, Whatman chromatographic paper No 3, 5 mm wide, was held horizontally in a Perspex tube, B (40 cm length), of a slightly larger diameter This tube had a small hole, K, in the centre through which ^{233}Pa was spotted on to the paper and the hole was covered later on with a close fitting PVC tubing The tube containing the paper strip as well as the electrolyte tanks, G, were cooled by immersion in a larger reservoir of ice cold water, H, as indicated in Fig 1 An electronically stabilized d c potential of 150 V was applied through graphite electrodes The potential gradient on the strip was 3 3 V/cm The current (30 to 40 mA) during any given run remained steady, showing that there were no changes in the conductivity

After the appropriate time interval, the current was switched off and the acid drained out from the electrode compartment The paper strip was dried by blowing warm air through the Perspex tube The strip was then cut in lengths of 1 cm and the activity of ^{233}Pa was measured on the scintillation spectrometer A blank experiment without the electrical potential being on, showed that ^{233}Pa diffuses to a maximum of 0 5 cm on either side of the neutral line

2 RESULTS AND DISCUSSION

2-1 *Effects of acidity in solvent extraction and electrophoresis studies*

In solvent extraction experiments, the molarity of HCl in the aqueous phase was varied from 3 0 to 5 5 M The results of studies of extraction into undiluted TBP and 5 and 25% TBP in benzene are shown in Fig 2 From this it is seen that, in all the

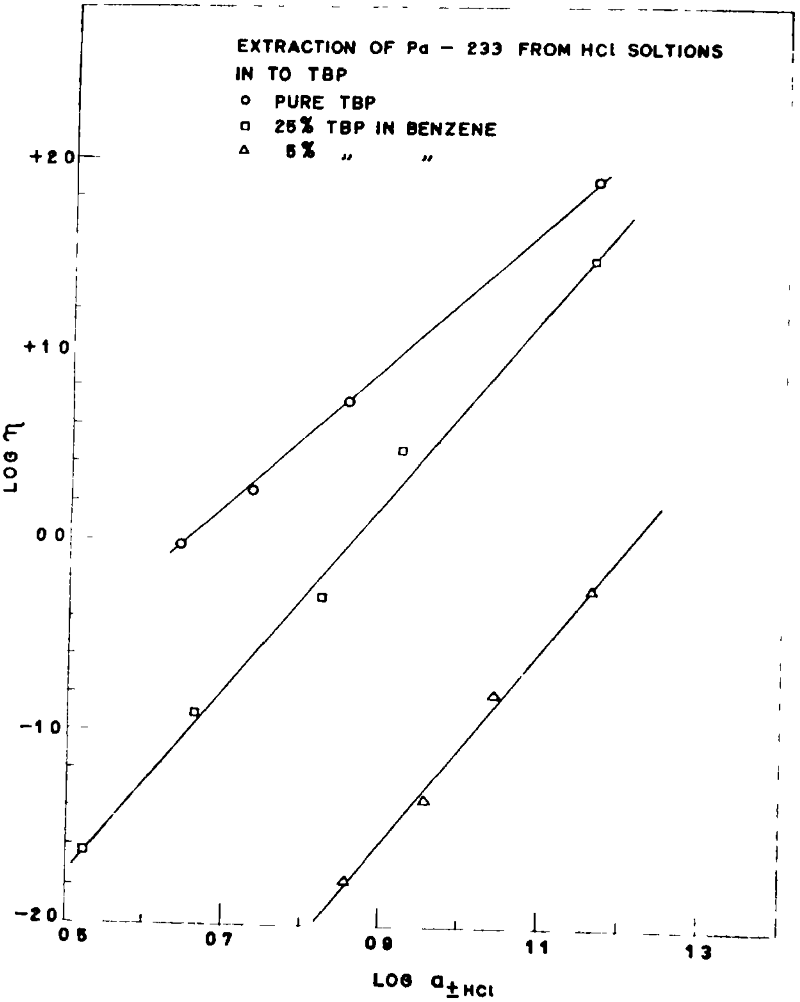


FIG 2—Extraction of ^{233}Pa from HCl solutions into TBP

three cases, the logarithm of the distribution coefficient (η) increases linearly with the logarithm of the activity of HCl The plots for 5 and 25% TBP are parallel and have a slope of five, while the slope of the plot for undiluted TBP is somewhat lower (~3 5)

In electrophoresis studies, the acidity was varied from 3 5 to 6 0 M HCl The histograms shown in Fig 3 are averages of at least three independent runs These clearly indicate that although a major fraction of protactinium (~70 per cent) remains at the centre line (neutral zone) the anion to cation ratio increases with increasing acid molarity

The nature of the protactinium species in aqueous acidic solutions has been the subject of study by several workers WELCH,[(10)] on the basis of ion exchange studies in perchloric acid suggested the existence of the protactinyl ion KRAUS,[(11)] and CASEY and MADDOCK[(2)] have however postulated partially hydroxylated species of protactinium It seems now generally accepted[(12)] that most of these species are of the type $[Pa(OH)_nX_m]^{(5-n-m)}$ Depending upon the values of n amd m, they are cationic, neutral or anionic and an equilibrium between these species is rapidly established in the solution [(2)] In solvent extraction studies (at a fixed solvent dilution), if the plots of the logarithm of the distribution coefficient against the logarithm of activity of the acid employed are linear one of the possibilities is that single species only is extracted, even though several species in dynamic equilibrium may be present in the aqueous phase For the extraction of ^{233}Pa into TBP, the log log plots (Fig 2) are linear The slope of five for plots for both 5 and 25% TBP can only be explained by postulating conversion of a highly hydroxylated species such as $Pa(OH)_4Cl^+$ into a readily extractable neutral species, $Pa(OH)Cl_4$ However, the slope of the log–log plot for pure TBP is of the order of 3 5 This can be accounted for as due to the extraction of a neutral species such as $Pa(OH)_2Cl_3$ formed from the same cation The latter neutral species having more hydroxyl groups cannot be expected to be extracted into diluted TBP

As has been stated earlier, in paper electrophoresis most of the protactinium (~70 per cent) is found to remain in the neutral zone Part of this may be neutral species An alternative reason for immobility is the hydrolytic polymerization of protactinium on contact with the paper ^{233}Pa is completely extractable from the stock solution into TBP (free from DBP) indicating that if polymer formation takes place it occurs only on contact with the paper * It is possible to gain an insight into the nature of the ionic species by examining the changing anion to cation ratios in Fig 3 (Strip No 1 on either side of the central line is regarded as the neutral zone, the remaining being cationic or anionic)

A general case of conversion of a cation into an anion by the removal of hydroxyl groups and addition of chloride ions can be represented by

$$[Pa(OH)_n(Cl)_m]^{(5-n-m)+} + xH^+ + yCl^-$$
$$\rightleftharpoons [Pa(OH)_{n-x}(Cl)_{m+y}]^{-[5-(n-x)-(m+y)]} + xH_2O$$

* This has been verified by absorbing a known amount of ^{233}Pa on a paper strip and determining the fraction of protactinium extractable at the end of 1 hr A major fraction (~70 per cent) remained inextractable

(10) G A WELCH, *Nature, Lond* **172**, 458 (1953)

(11) K A KRAUS, *The Proceedings of the International Conference on the Peaceful Uses of Atomic Energy* Geneva 1955, Vol 7 p 245 United Nations (1956)

(12) V A MIKHAILOV, *Russ Chem Rev* , **29** (7), 419 (1960)

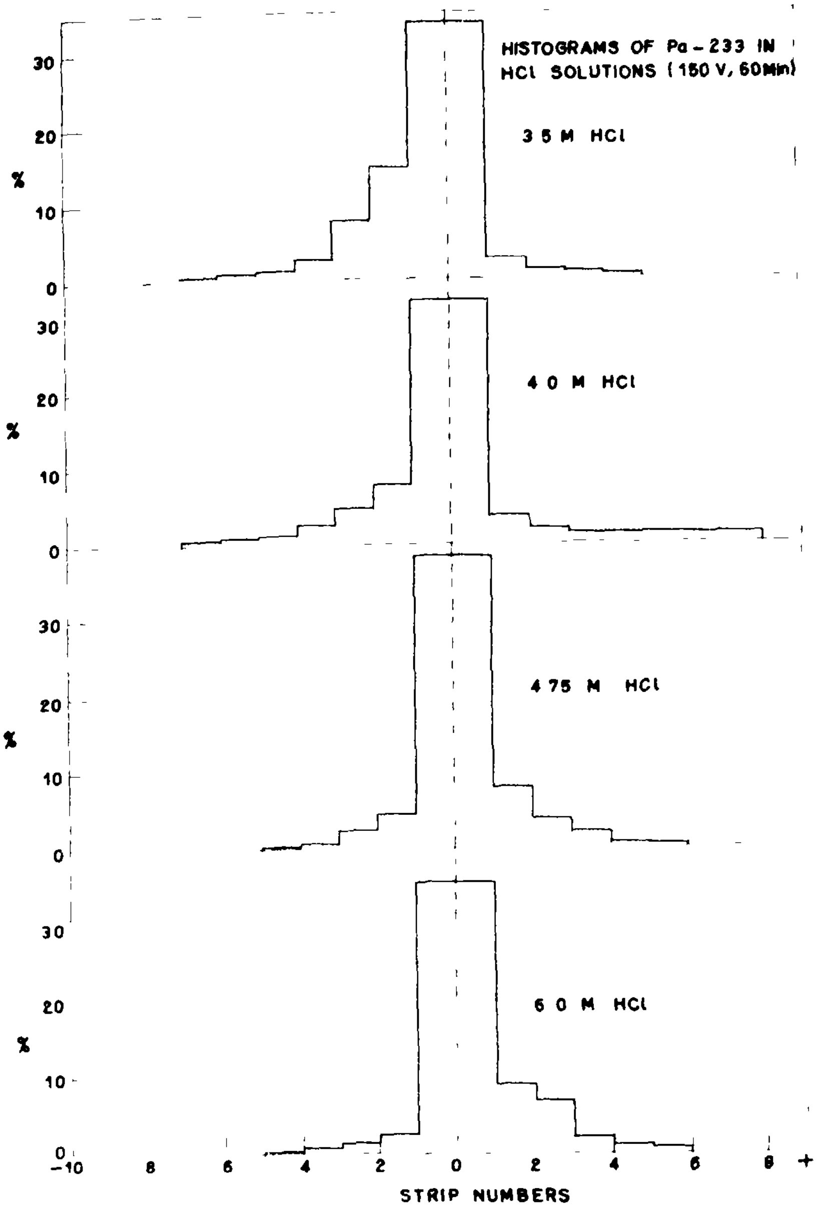


FIG. 3.—Histograms of ^{233}Pa in HCl solutions

The equilibrium constant is given by

$$K = \frac{(\text{Anion})}{(\text{Cation})\,(\text{H}^+)^x\,(\text{Cl}^-)^y} \tag{2}$$

Assuming the anion to cation ratio obtained in electrophoresis studies to be q Equation (2) reduces in HCl solutions to,

$$K = \frac{q}{(\text{HCl})^{x+y}} \tag{3}$$

or

$$\log q = (x + y)\log(\text{HCl}) + \log K \tag{4}$$

A plot of log q against log (HCl) will be linear if only one cation to anion conversion is involved, the slope giving the value $(x - y)$. Since strong HCl solutions are employed in the present study, it will be more realistic to plot log q against log $a_{\pm HCl}$ rather than log M HCl. When x and y are not equal, using $a_{\pm HCl}$ will of course be an approximation.

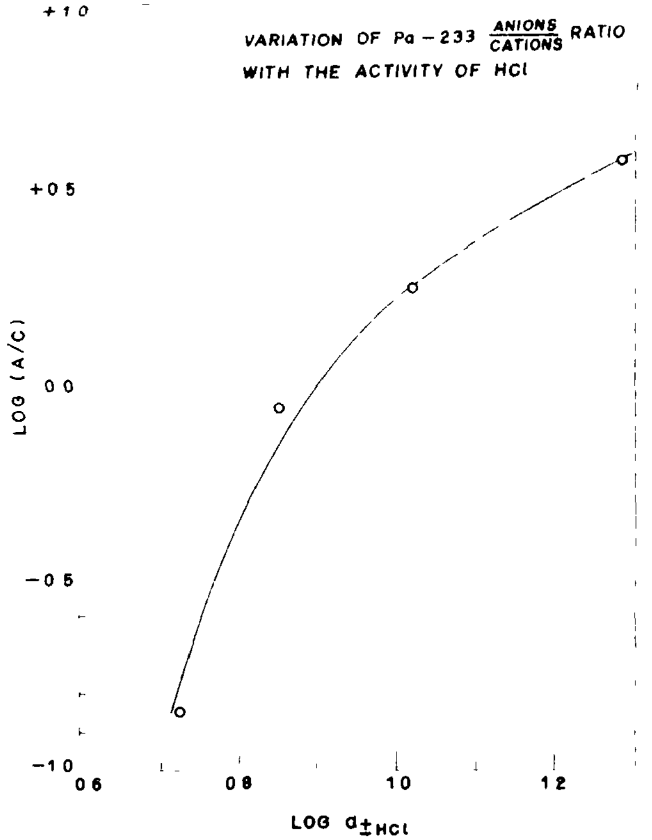


Fig. 4 Variation of ^{233}Pa anions/cations ratio with the activity of HCl

The plot of log q against log $a_{\pm HCl}$ in the present studies is shown in Fig. 4. Since this is a smooth curve, it is evident that more than one cation to anion conversion is involved. The maximum slope of this curve is found to be six. If the cations of protactinium are unipositive and the anions uninegative, only even number values of slopes, viz., 2, 4, and 6, are meaningful. Some of the possible conversions with these values of slope are

(a) $Pa(OH)_3Cl^+$ to $Pa(OH)_2Cl_4$ or $Pa(OH)Cl_5$

(b) $Pa(OH)_2Cl_2^+$ to $Pa(OH)_2Cl_4$ or $Pa(OH)Cl_5$ or $PaCl_6$

(c) $Pa(OH)Cl_3^+$ to $Pa(OH)Cl_5$ or $PaCl_6^-$

Thus one can explain the results of solvent extraction and electrophoresis studies by assuming a number of species of protactinium in aqueous HCl solutions.

Besides the species of protactinium postulated by Casey and Maddock[2], viz. $Pa(OH)Cl_3^+$, $Pa(OH)_2Cl_3$, $Pa(OH)Cl_4$, $Pa(OH)_2Cl_4$, $Pa(OH)Cl_5$ and $PaCl_6^-$ two other species have to be postulated to fully account for the results of paper electrophoresis These can be formulated as $Pa(OH)_3Cl^+$ and $Pa(OH)_2Cl_2^-$

2-2 *Effect of complexing agents in solvent extraction and paper electrophoresis of* ^{233}Pa

The effects of the addition of hydrofluoric, phosphoric and citric acids in the extraction *of ^{233}Pa from 3.5 M HCl solutions into 25% TBP in benzene, are illustrated in Fig 5 In these graphs, the ratio of the distribution coefficients in the presence and absence of complexing agents, is plotted against the molarity of the complexing agents The fluoride ion has a very marked depressing effect on the extraction of ^{233}Pa as* compared to the phosphate

The effects of the addition of hydrofluoric acid and citric acid on the migration of ^{233}Pa in paper electrophoresis experiments are shown in Fig 6 Compared to the control sample of ^{233}Pa in 3.5 M HCl the addition of HF has produced a remarkable change in the histogram ^{233}Pa species in the neutral zone are reduced from 70 to 10 per cent (in a 25 min run) and then eventually disappear in longer runs On the whole, the mobility of ^{233}Pa increases considerably and a clear cationic peak is observed Roughly equal amounts of activity appears as cations and anions

Thus the changes in the behaviour of ^{233}Pa on addition of HF are remarkable both in solvent extraction and electrophoresis These results undoubtedly indicate the formation of strong complexes, both cationic and anionic at the expense of the neutral species This may be the reason for the suppression of the extraction of ^{233}Pa into 25% TBP These complexes may be of the general type $[Pa(OH)_nF_xCl_y]^{5-(n+x+y)}$ To a limited extent, the behaviour of ^{233}Pa in the presence of phosphate is also similar The tendency of protactinium towards hydrolytic polymerization on contact with paper, is completely suppressed by HF(1) This is probably the result of the substitution of the bridge-forming OH groups by fluoride

As seen from Fig 5, the behaviour of ^{233}Pa in the presence of citric acid is different from that of fluoride and phosphate The results are similar to those obtained by CASEY and MADDOCK(2) using oxalic acid At very low concentration of citric acid (0.005 M), there is an increase in the extraction This is followed by a gradual decrease with increasing concentration of citric acid Similar experiments with tartaric and lactic acids in the aqueous phase did not show any variation in the distribution coefficients up to a concentration of 0.04 M of these acids

In paper electrophoresis studies, when citric acid is used as the complexing agent increased mobility of protactinium is once again observed (Fig 6) The changes in the percentage distribution of ^{233}Pa in cationic neutral and anionic forms in the presence of citric acid are given in Table 1

TABLE 1

Electrolyte	Percentage of ^{233}Pa in the form of Cations	Neutral	Anions
1 3.5 M HCl	28.0	68.0	4.0
2 3.5 M HCl + 0.005 Citric acid	16.0	50.0	34.0
3 3.5 M HCl + 0.1 M Citric acid	17.0	76.0	7.0

The effects of citric acid are thus more complex as compared to those of the inorganic ions A possible explanation of the behaviour of ^{233}Pa in HCl-Citric acid

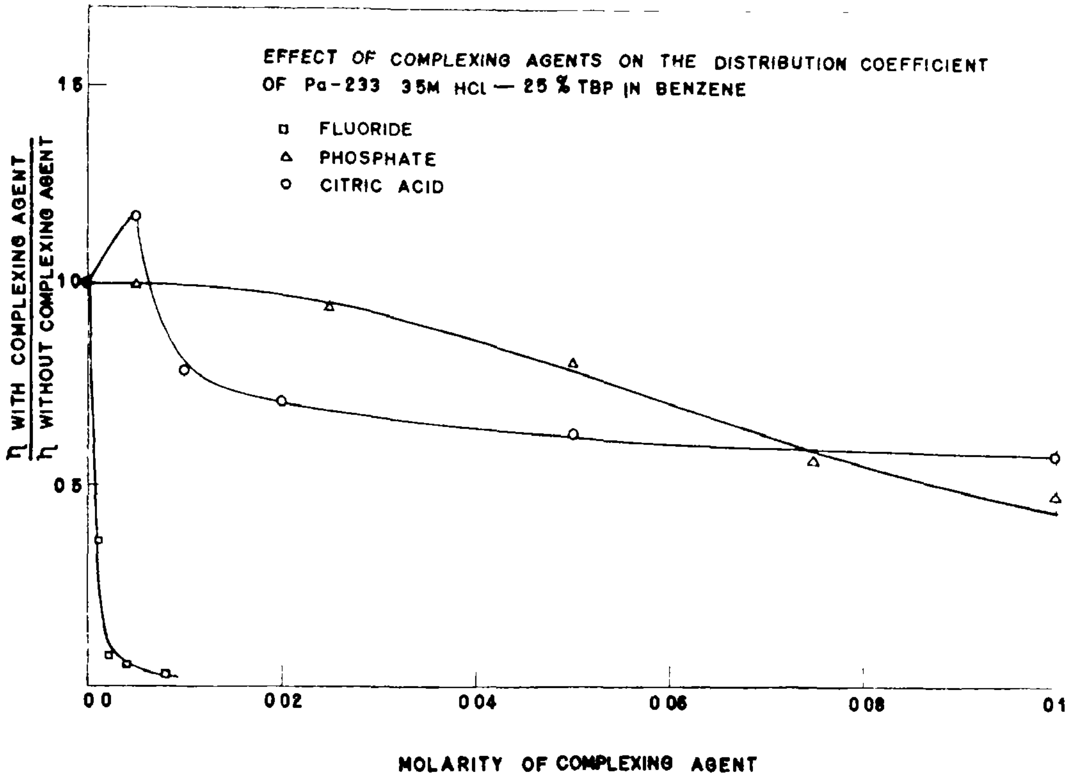


FIG 5 —Effect of complexing agents on the distribution coefficient of ^{233}Pa

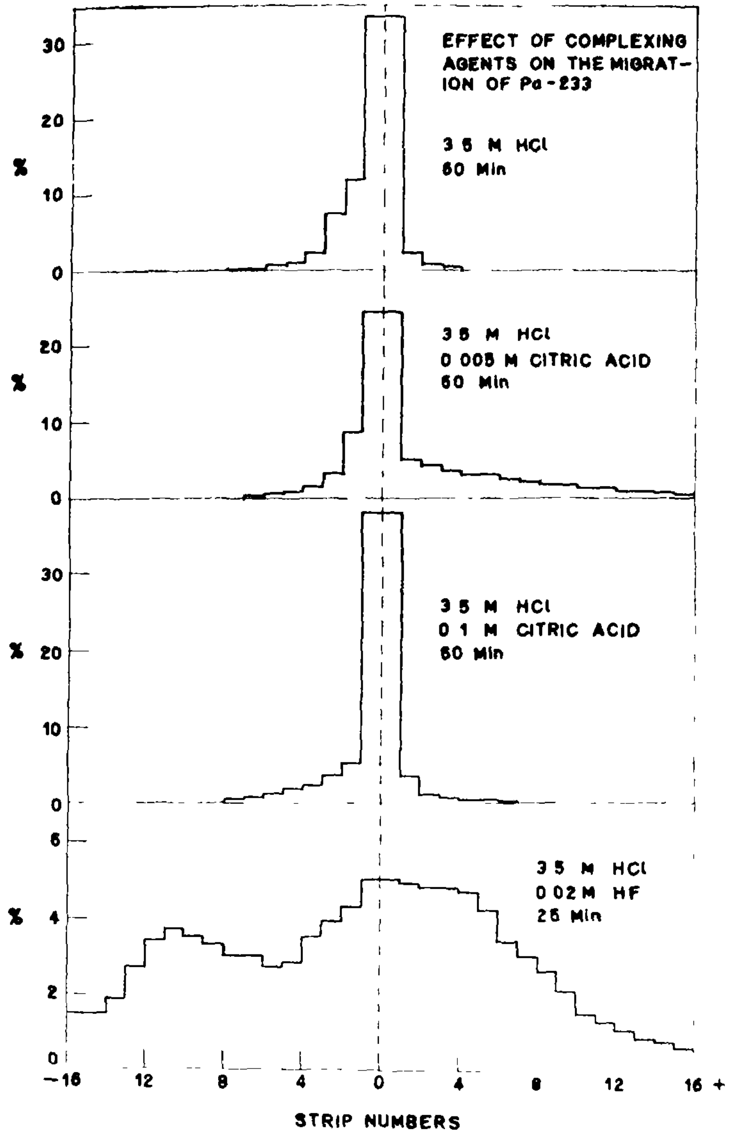


Fig. 6 — Effect of complexing agents on the migration of ^{233}Pa

mixtures depends upon the formation of different complexes In the presence of 0 005 M citric acid, a 30 per cent increase in the anions is observed This may be due to the prevention of hydrolytic polymerization by citric acid resulting in the formation of mobile anionic species (e g Pa(H_2 cit)Cl_3) However, as seen from Table 1, the decrease in the percentage of the species in neutral zone is only 18 instead of 30 per cent This may be due to the conversion of 12 per cent of the cations to the neutral species having one citrate group (e g Pa(OH)(H_2 cit)Cl_2) The formation of such neutral species will also account for the initial increase in extraction Further addition of citric acid (0 1 M) sharply reduces the extraction and mobility of protactinium due to the formation of complexes containing two or more molecules of citric acid which being heavy are much less mobile and less extractable as they are more hydrophilic in character.

2-3 *Extraction of ^{233}Pa by ethyl acetoacetate*

Ethyl acetoacetate has been found to be a good extracting agent. However, the reproducibility of the measurements was low. The concentration of hydrochloric acid was maintained at 6.0 M and 2 and 25 per cent ethylacetoacetate in benzene were tried. This average distribution ratios were found to be 0.032 and 0.6 respectively. However, the ratio for the extraction of ^{233}Pa into undiluted solvent was 8.0.

J. Inorg Nucl Chem 1963, Vol 25, pp 67 to 74 Pergamon Press Ltd Printed in Northern Ireland

THE REACTION OF ZIRCONIUM HALIDES WITH SOLUTIONS OF POTASSIUM AND POTASSIUM AMIDE IN LIQUID AMMONIA

M Allbutt and G W A Fowles
Chemistry Department, University of Southampton

(*Received* 16 *April* 1962, *in revised form* 22 *June* 1962)

Abstract—Conductiometric titrations have shown that the reaction of zirconium(IV) bromide with potassium amide in liquid ammonia corresponds to a final molar ratio $ZrBr_4$ KNH_2 1 0 6 0 Three products have been characterized, zirconium imide $Zr(NH)_2$ mono-potassium ammonozirconate, $Zr(NH)(NK)$, and di-potassium ammonozirconate, $Zr(NK)_2 2NH_3$ In the reaction of zirconium(IV) bromide with potassium solutions the end point occurred at a molar ratio $ZrBr_4$ K - 1 0 4 5 For the reaction of zirconium(III) bromide with potassium amide a molar ratio $ZrBr_3$ KNH_2 1 0 3 5 was found An intermediate product containing zirconium in the average oxidation state of 3 5 is proposed

When zirconium(IV) chloride reacts with liquid ammonia an ammonobasic zirconium(IV) chloride is precipitated, although a small amount of a soluble zirconium compound is also formed Thus Fowles and Drake(1) found that the insoluble product (after six washes with liquid ammonia at 35 C) had a composition corresponding to Zr Cl N 1 00 2 90 6 04, indicating that only one zirconium–chlorine bond was ammonolysed, some 7 per cent of the zirconium was found in the collected filtrates but this increased to 33 per cent when the insoluble product was heated *in vacuo* to 100 C between washes, the insoluble material then having the composition Zr Cl N 1 00 2 54 5 08 It was conjectured that the presence of soluble zirconium species resulted from complex formation by ammonium chloride liberated in the primary ammonolysis, e g

$$ZrCl_4 \quad yNH_3 \rightarrow ZrCl_3(NH_2)\,xNH_3 \quad NH_4Cl \tag{1}$$

$$ZrCl_3(NH_2).xNH_3 \quad 2NH_4Cl \rightarrow (NH_4)_2[ZrCl_5(NH_2)] \tag{2}$$

The data were, however, insufficient to indicate the nature or extent of this complex formation

From the analogous ammonolysis of zirconium(IV) bromide at room temperature Bowermann and Fernelius(2) obtained an insoluble product with Zr Br N 1 00 2 33 5 82, addition of a solution of potassium gave a black precipitate and a red solution Young(3) had earlier reported a similar observation and noted that the precipitate became white with excess of potassium

The initial black precipitate was suspected to contain lower-valent zirconium, though this was not proved Addition of amide ion caused replacement of bromine with eventual formation of dipotassium ammonozirconate $Zr(NK)_2 2NH_3$ however intermediate products representing partial replacement could not be isolated in a pure form

The titration techniques developed by Watt and co-workers(4) seemed applicable to this system, since it was observed that the amide catalysis which occurs when solutions of alkali metals react with halides of nickel[5] and iron[6] does not take place with zirconium.

---

(1) G W A Fowles and J E Drake, *J Less Common Metals*, **2**, 401 (1960)

(2) F W Bowerman and W C Fernelius *J Amer Chem Soc* **61**, 121 (1939)

(3) R C Young *J Amer Chem Soc* **57**, 1195 (1935)

(4) G W Watt and C W Keenan, *J Amer Chem Soc* **71**, 3833 (1949)

We have accordingly developed conductiometric procedures and used them to titrate the ammonolysis products with solutions of potassium and of potassium amide.

EXPERIMENTAL

Though WATT's apparatus had the merit of versatility, its intricacy and use of liquid ammonia as a refrigerant were considered too hazardous for regular manipulations. Design was governed mainly by the need for an evacuable system to allow ammonia to be distilled and anhydrous conditions maintained together with provision for a positive gas pressure to force solutions from the burette into the titration cell. This was achieved by connecting the heads of burette and titration vessel to a twin-manifold system (cf. Fig. 1).

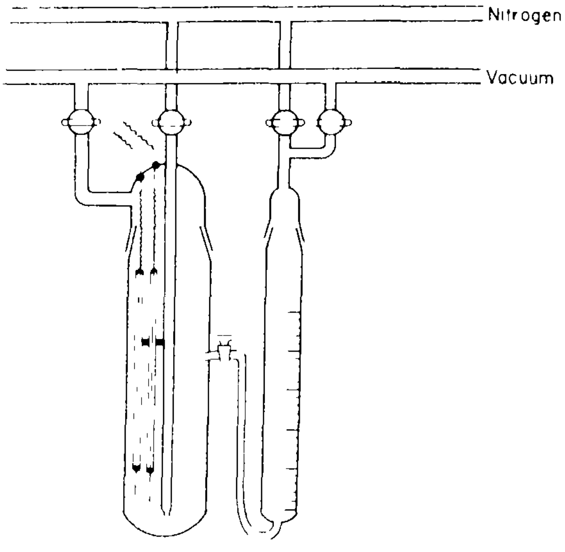


FIG. 1.—Titration apparatus.

One manifold lead to a vacuum and mercury diffusion pump, and through it dry ammonia was distilled into the apparatus; the other supplied dry oxygen-free nitrogen at a pressure slightly above atmospheric. The cell and burette were immersed in an acetone Drikold bath (−40 to −50°C) and contained in a wide-necked unsilvered Dewar to a depth such that the barrel of the stopcock was about half submerged. Levels of solution in burette and titration cell were maintained below the level of acetone.

Increments of solution were run from the burette by applying pressure from the nitrogen manifold to the head of the burette with the titration cell vented to the atmosphere through a drying tower. At the same time the titrated solution was stirred by flushing nitrogen through the inlet tube passing to the bottom of the titration cell. Bright platinum electrodes, positioned by attachment to this tube, had connecting leads passing to the exterior through metal-glass seals in the head of the titration cell and enabled the conductivity to be continuously measured.

Preparation of solutions of alkali metals and potassium amide

By means of modified version of the procedure described by DOSTROVSKY and LLEWELLYN[7], the alkali metals (sodium and potassium) were purified and stored in narrow glass tubes. As required, short segments were cut from the middle of the tubes, weighed and transferred to the burette; negligible oxidation occurred. A known weight of the zirconium halide was then added to the titration vessel against a counter-current of nitrogen, and anhydrous ammonia was distilled into both the burette and titration vessel and the resulting solutions equilibrated with the cold bath. During the subsequent titration, the temperature of the acetone was maintained to ±1°C by periodic additions of small quantities of crushed Drikold

---

[5] G. W. WATT, W. F. ROPER and S. G. PARKER, *J. Amer. Chem. Soc.* **73**, 5791 (1951).

[6] G. W. WATT and W. A. JENKINS, *J. Amer. Chem. Soc.* **73**, 3275 (1951).

[7] I. DOSTROVSKY and D. R. LLEWELLYN, *J. Soc. Chem. Industr.* **68**, 202 (1949).

When a solution of potassium amide was required, a short length of partly-rusted iron wire was also placed in the burette, and this caused complete conversion of the potassium solution in about 2 hr at -40°C

Isolation and analysis of products

Products formed in the various titrations were isolated by means of a suitable vacuum filtration [8] Zirconium, halogen and nitrogen were determined as described previously [1] Sodium and potassium were estimated as normal anhydrous sulphates by addition of sulphuric acid to the filtrate from the zirconium determination and evaporation to dryness, the residues were ignited at 500°C with ammonium carbonate

RESULTS

1 *Reaction of Alkali Metal Solutions with Zirconium*(IV) *Halides*

(i) *Conductiometric titrations*

Titrations were carried out using freshly-formed suspensions of the ammonolysis products, since separated ammonobasic zirconium(IV) halides appeared to react only slowly and incompletely Similar conductance changes were observed for zirconium (IV) chloride and bromide with either potassium or sodium metal solutions Fig 2(a) shows a typical plot obtained by the titration of the bromide with potassium, the capitals A, B, C, etc refer to the visual appearance of the contents of the titration vessel

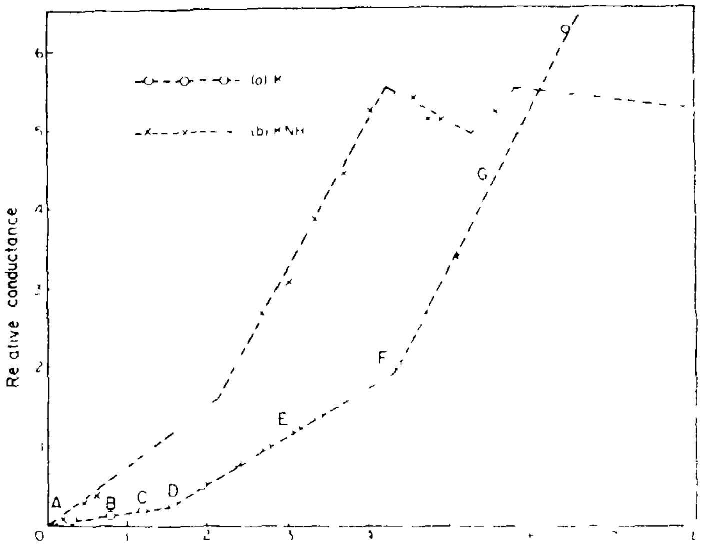


Fig 2 —Reaction of $ZrBr_4$ with (a) K and (b) KNH_2

Fig 2(a) shows that the titration proceeds in two stages The initial reaction of potassium should be with the NH_4^+ ions, but the immediate appearance of a brown colour indicates that the soluble zirconium species is also involved

The second stage involves reaction with the insoluble ammonobasic zirconium(IV) bromide, since this disappears and is progressively replaced by the brown precipitate

---

[8] G W A Fowles and F H Pollard, *J Chem Soc* 2588 (1953)

TABLE 1. APPEARANCE OF PRODUCTS OF $ZrBr_4$–K REACTION

	Stage	Appearance		Conductance
		Solution	Precipitate	
A	Initial	Colourless	White (granular)	Slow change with time
B	First addition of K	Brown	White (granular)	Steady
C and D	Further addition of K to first endpoint	Darker brown	White (granular) with an additional brown (flocculent)	Steady
E	Between first and second endpoints	Brown	White (granular) now dissolving producing brown	Steady only after 2–3 min
F	Second endpoint	Brown	Black (granular)	Steady
G	After second endpoint	Blue	Black (granular)	Steady

TABLE 2. RESULTS OF ZrX_4–M TITRATIONS

Titration	Temperature (°C)	Ratio ZrX_4:M	
		First endpoint	Second endpoint
Na–$ZrBr_4$ (1)	53	1.00:1.57	1.00:4.57
(2)	57	1.00:1.68	1.00:4.58
K–$ZrBr_4$ (1)	40	1.00:2.16	1.00:4.51
(2)	42	1.00:1.48	1.00:4.56
Na–$ZrCl_4$	45	1.00:1.61	1.00:4.58

(ii) *Isolation of products*

Reactions were carried out using various ratios of reactants.

(a) *Using less than four equivalents of* K. The black granular precipitate was filtered, washed thoroughly with liquid ammonia at −35°, and then warmed *in vacuo* to 40°C for 1 hr, when it became grey in colour. The soluble product was a heterogeneous mixture of white and red-brown solids. Both products were diamagnetic, and titration with ceric sulphate solution showed the zirconium to be in the quadrivalent state, e.g. valence states of 3.94 and 3.95 were found.

(b) *Using between* 4 *and* 4.5 *equivalent of* Na. A colourless solution was formed together with the usual black solid, the latter became pale yellow *in vacuo* at room temperature. [Found (for product formed with 4.5 equivalents): Zr, 70.2, Cl, 2.6

TABLE 3.—ANALYTICAL DATA FOR $ZrBr_4$–K/NH_3 REACTIONS

Experiment	*Zr* (%)	*Br* (%)	N (%)	K (%)	*Zr*	*Br*	N	K
1 *Insoluble* product	63.9	13.6	20.0	—	1.00	0.24	2.04	—
2 Insoluble product	50.5	27.8	18.2		1.00	0.63	2.34	-
Soluble product	7.4	63.4	5.4	23.3	1.02	9.8	4.7	7.3

N, 21.2, Na, 5.1%, corresponding to Zr:Cl:N:Na = 1.00:0.10:1.96:0.41] The filtrates contained only sodium chloride.

(c) *Using excess* (4.5 *equivalents of* Na *or* K. The only products isolated from the reactions were diamagnetic and pale yellow. The isolation procedure (pumping at room temperature) evidently resulted in the formation of amide which interacted further with the zirconium product. Such amide formation did not take place in the titration, however, since the blue colour persisted and the conductance remained steady after the second end-point.

Since sodium amide is almost insoluble in ammonia its presence could be confirmed by analysis, e.g. Zr, 39.9, N, 25.9, Na 32.4%, corresponding to Zr:N:Na = 1.00:5.08:3.22 and Zr, 26.4, N, 32.3, Na, 36.6%, corresponding to Zr:N:Na = 1.00:7.96:5.69.

The analogous reaction of zirconium(IV) bromide with potassium gave a pale yellow product whose composition corresponded approximately to the monopotassium salt (Found: Zr, 51.8, N 17.6, K 28.0%, corresponding to Zr:N:K = 1.00:2.21:1.26).

2. *Reaction of Potassium Amide Solutions with Zirconium*(IV) *Bromide*

(i) *Conductiometric titrations*

The conductance plot given in Fig. 2(b), shows two main endpoints, the second of which is rather poorly defined and characterized by a multiplicity of inflexion points, two downward and one upward. The first stage again involves the soluble zirconium species, since a white flocculent precipitate appears immediately upon addition of amide, and the final inflection point corresponds to the formation of dipotassium ammonozirconate, $Zr(NK)_2 \cdot xNH_3$.

The slow decrease in conductance observed on addition of excess of potassium amide must arise because the dilution effect is greater than the contribution of the amide to the conductance.

(ii) *Isolation of products*

A solution of potassium amide was added to a suspension of the ammonolysis products formed by zirconium(IV) bromide, and after agitation the products were filtered, washed six times with ammonia, and finally pumped under vacuo for 2 hr at 50°.

3 *Reactions of Zirconium*(III) *Bromide*[7]

Zirconium(III) bromide was prepared in small amounts by the reduction of zirconium(IV) bromide with hydrogen in a glow discharge (9) (Found Zr, 27 8, Br, 72 6, μ, 0 7 B M Calc for $ZrBr_3$ Zr, 27 5 Br, 72 5%) Larger quantities were obtained by carrying out the reduction with aluminium in a sealed tube at 380°C

(i) *Reaction with* KNH_2

Zirconium(III) bromide reacted with liquid ammonia to give a dark brown precipitate and a brown solution The changes in conductance observed upon the addition of potassium amide are shown in Fig 3(b) A blue colour formed locally in the first stages of the reaction but disappeared when dispersed throughout the body of the

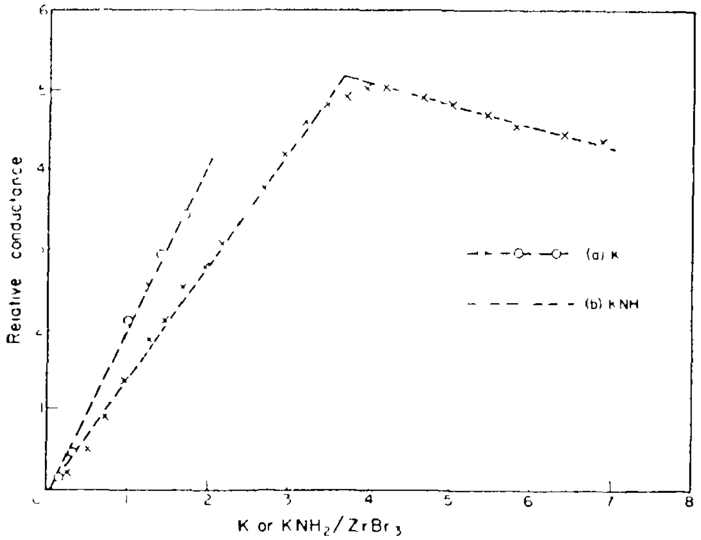


Fig 3 Reaction of $ZrBr_3$ with (a) KNH_2 and (b) K

solution, causing formation of an additional flocculent brown precipitate Near the maximum point, the blue colour persisted throughout the solution and remained when excess of amide was added By this stage the precipitate was black and granular

This black precipitate was filtered and washed with ammonia, but on pumping for 30 min at 40 C the product became grey in colour It was diamagnetic and did not decolourize potassium permanganate (Found Zr, 41 9, N, 20 9, K, 30 2%, corresponding to Zr N K = 1 00 3 25 1 69) The presence of potassium in the soluble portion was confirmed by the vigorous evolution of hydrogen that took place upon the addition of ethanol

(ii) *Reaction with* K

The conductance plot obtained from a typical experiment is shown in Fig 3(a) The steady rise in conductance took place concurrently with the discharge of the blue colour and the formation of a dark brown precipitate After the addition of approximately two equivalents of potassium, the blue colour seemed to persist, only to fade again after several minutes, at the same time, gas bubbles were formed and the conductance decreased gradually with time Evidently amide formation was taking place, and this observed the precise endpoint With a large excess of potassium, the blue colour persisted and the conductivity remained constant

---

(9) I F Hewmann and J A Watts, *J Amer Chem Soc* **82,** 2113 (1960)

DISCUSSION

Studies of the hydrolysis of zirconium(IV) halides in acid solutions have shown that soluble zirconium species are present as polymers whose complexity depends on the pH of the solution Corresponding experiments have not been made in liquid ammonia because of the difficulty of applying the appropriate techniques, e g spectrophotometry(10) and measurement of diffusion coefficient,(11) but nevertheless since polymerization increases with pH in aqueous solutions, then the zirconium species formed in liquid ammonia—a more basic solvent—must also be polymerized Furthermore, the imide $Zr(NH)_2$ must be polymerized unless the zirconium atoms have a co-ordination number of two (12) By analogy with ZrO_2, the imide probably has a three-dimensional structure with Zr NH Zr bridges, the lone pair of electrons on the nitrogen atoms is likely to be donated to near-by zirconium atoms, thus increasing the degree of polymerization and making the hydrogen atom acidic in character The experimental results may be integrated on the basis of such polymeric models

(a) *Acid base reactions with potassium amide*

The addition of amide ion first removes any ammonium ions in solution and then displaces bromine atoms from the individual zirconium units of the ammonobasic zirconium(IV) bromide polymer

$$ZrBr_3NH_2 + NH_2^- \rightarrow [ZrBr_3(NH_2)_2]^- \rightarrow$$
$$ZrBr_2(NH_2)_2 + Br^- \rightarrow \quad \rightarrow Zr(NH_2)_4 \rightarrow Zr(NH)_2 + 2NH_3$$

A gradual rise in conductance is observed during this stage (cf Fig 2)

The acidic nature of the hydrogen atoms in zirconium(IV) imide results in the formation of potassium derivatives The mono-potassium derivative forms first of all, and the conductance of the solution falls accordingly The conductance increases again as the di-potassium derivative begins to form, showing that additional ionic species are being formed, moreover, at least two additional molecules of ammonia are co-ordinated to zirconium in the di-potassium ammonozirconate These observations suggest that the polymeric structure is largely broken down by an excess of potassium amide, with the formation of ionic species

$$Zr(NH)(NK) \xrightarrow{KNH_2} Zr(NK)_2\,2NH_3$$
$$K_2[Zr(NH)_2(NH_2)_2] \xrightarrow{KNH_2} K_2[Zr(NH_2)_6]$$

(b) *Oxidation -reduction reactions with alkali metals*

Although the reactions of zirconium(IV) halides with alkali metals resemble those with the amides, in that all four halogen atoms are displaced they differ in that the final endpoint occurs at a lower molar ratio (the values being 4 5 and 6 respectively)

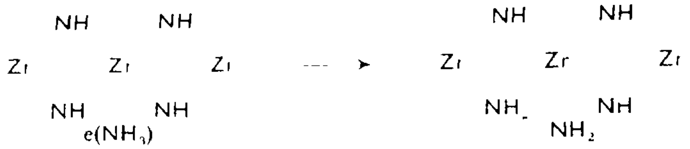
---

(10) A J Zielen and R E Connick *J Amer Chem Soc* **78**, 5785 (1956)
(11) D A Williams-Wynn *J Phys Chem* **63**, 2065 (1959)
(12) W B Blumenthal *Industr Engng Chem* **46**, 528 (1954)

A possible explanation is that although the imide is formed in both reactions, s reduction of zirconium then takes place with excess of alkali metal Since the lo valent zirconium is more basic it will be less likely to undergo an amphoteric react. The reaction of zirconium(III) bromide with potassium amide, on the other ha

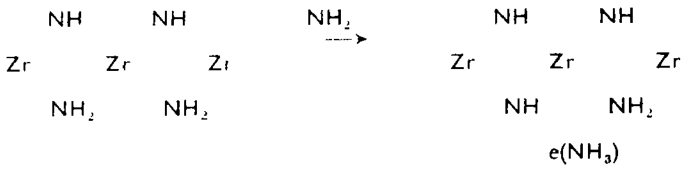
The reaction of zirconium(III) bromide with potassium amide, on the other ha gives a product whose oxidation state is greater than 3, the liberation of potass metal indicates that the reduction potential of zirconium(III) is more negative t that of potassium (cf the similar reducing power of molybdenum(III) bromide report by Bergstrom(13)) Moreover the polarographic wave of zirconium(IV) in liqui ammonia shows no reduction step at potentials less negative than for potassium (1

A consistent pattern develops if we assume that in all the reactions an average oxidation of 3 5 is present We tentatively suggest that the polymeric nature of the imide is largely retained and that alternate zirconium atoms are reduced by the nucleophilic attack of an ammoniated electron on a Zr N bond



The alternating sequence of Zr(IV) and Zr(III) states would account for the intense black colour of the product

A directly analogous compound would result from the oxidation of the product of the zirconium(III) bromide-potassium amide reaction



We should expect one potassium atom to be taken up by every other zirconium atom

Acknowledgement—We much appreciate the support given this work by the Department of Scientific and Industrial Research through a special research grant

(13) F W Bergstrom *J Amer Chem Soc* 47, 2317 (1925)

(14) G W A Fowles and M Allbutt, Unpublished observations (1961)

[illegible]rg. Nucl. Chem., 1963, Vol. 25, pp. 75 to 78. Pergamon Press Ltd. Printed in Northern Ireland

A LOW TEMPERATURE SYNTHESIS FOR POWDER-FORM INTERMETALLICS AND OTHER COMPOUNDS—II

SELENIDES

S. M. KULIFAY
Research and Engineering Division, Monsanto Chemical Co., St. Louis,
Missouri

(Received 9 May 1962, in revised form 18 June 1962)

Abstract—*The work previously reported by* KULIFAY *has been extended to include selenides of which nine have been prepared including* $CuSe$, βAg_2Se, $CdSe$, $PbSe$, $TlSe$, $HgSe$, $NiSe$, $Cu_{2-x}Se$ *(where* $x \sim 0.2$*) and* $CuAgSe$. *As was the case with intermetallics, antimonides, arsenides and tellurides the selenide synthesis is quantitative, simple and rapid, and uses a temperature of only 100°C at atmospheric pressure. It consists of the reduction of mixed aqueous solutions containing the elements in the stoicheiometric ratio called for in the product, by addition to aqueous ammoniacal hydrazine solutions. Two copper selenides can be prepared by varying the elemental proportions.*

THE writer developed[1] a general method for the synthesis of intermetallics, antimonides, arsenides and tellurides, and it was desired to determine the extent to which the method would apply further, specifically with selenides.

BENZING *et al.*[2] have published work, in which of all selenides prepared but one they first isolated the solid metal selenite before reducing with hydrazine. In preparing zinc and cadmium selenides, they formed first a hydrazinometal selenide complex which was then decomposed with acetic acid before obtaining the normal selenide. The current work extends previous work to the preparation of selenides of silver, thallium, nickel and the ternary CuAgSe, in addition to PbSe, CdSe, CuSe, $Cu_{2-x}Se$ (where $x \sim 0.2$), and HgSe, and provides a simpler method by bypassing the intermediate steps.

EXPERIMENTAL AND RESULTS

Apparatus and procedure. Separate solutions (A) and (B) of the starting metals or compounds indicated in Table 1 were prepared in covered 150 ml beakers. These solutions were then poured together, rinsing to complete the transfer. This mixture was swirled well, resulting in a clear homogeneous solution of the two metal ions in the exact stoicheiometric ratio desired. The reducing solution indicated was made up in a covered 1 l. beaker and heated to boiling. Just as the boiling temperature was reached the metals solution was added carefully in a fine stream with constant stirring and rinsing. The reduction was immediate, and vigourous in the case of the Cu and Hg compounds where much gas was evolved. The reduction beaker was covered and the contents boiled 1.5 hr, except where otherwise indicated in Table 1, rinsing down occasionally any precipitate which accumulated above the liquid. This was then suction-filtered through an oven-dried, tared, sintered-glass filtering crucible. It was washed well, then drained by suction. This was rinsed with methanol and air-dried at 70°C to constant weight. The products are susceptible to oxidation at higher temperatures.

Materials. All raw materials were B and A Reagent quality or equivalent. Where Hg element was used, its HNO_3 solution was heated after solution was complete, to insure oxidation to Hg (II). This would lessen hydrolytic precipitation at the stage where the metals solutions were rinsed together prior to adding to the reducing solution. Equivalent amounts of HgO may be used instead of Hg for ease in weighing, and to eliminate the above extra heating.

---

[1] S. M. KULIFAY, *J. Amer. Chem. Soc.* **83**, 4916–19 (1961).

[2] W. C. BENZING, J. B. CONN, J. V. MAGEE and E. J. SHEEHAN, *J. Amer. Chem. Soc.* **80**, 2657–59 (1958).

Table 1

Compound and formula	[illegible]	Composition of reducing solution	% Yield and X-ray diffraction ana
Selenides *Cupric selenide (klockmannite)* *CuSe*	(A) [illegible] g Cu in 4 ml 1 1 HNO_3 (B) 0 7896 g Se in 9 ml 2 1 HNO_3	5 g N_2H_4 2HCl 100 ml H_2O 50 ml NH_4OH	99 6% Agreed quite well with ASTM data for CuSe with no other detectable crystalline components present
silver selenide (naumannite) Ag_2Se	(A) 3 3979 g $AgNO_3$ in 15 ml H_2O followed by 10 ml NH_4OH (B) 0 7896 g Se in 9 ml 2 1 HNO_3 followed by 15 ml NH_4OH	15 g N_2H_4 2HCl 150 ml H_2O 50 ml NH_4OH	99 5% The only detectable crystalline component was Ag_2Se, which gave a strong pattern
Cadmium selenide CdSe	(A) 1 7242 g $CdCO_3$ in 6 ml 1 1 HNO_3 (B) 0 7896 g Se in 9 ml 2 1 HNO_3	5 g N_2H_4 2HCl 100 ml H_2O 50 ml NH_4OH	99 8% The major reflexions could be indexed as a FCC structure with $a_0 \sim$ 6 03 Å in agreement with Hansen[4] for cubic CdSe The crystallite size was very small and there were no detectable free elements
Lead selenide (clausthalite) PbSe	(A) 2 2321 g PbO in 15 ml 1 2 HNO_3 (B) 0 7896 g Se in 9 ml 2 1 HNO_3	3 g tartaric acid 15 g N_2H_4 2HCl 150 ml H_2O 50 ml NH_4OH	100 7% The only detectable crystalline component was PbSe, giving a very strong pattern The pattern was identified by comparison to PbSe data in NBS Circ 539, Vol V, p 38 (1955)
Thallium selenide TlSe	(A) 2 3191 g Tl in 25 ml 1 4 HNO_3 (B) 0 8940 g Se in 9 ml 2 1 HNO_3	15 g tartaric acid 15 g N_2H_4 2HCl 150 ml H_2O 65 ml NH_4OH	95 9% The sample gave a strong pattern, body centred tetragonal, with c/a 0 87, which compared favourably with Pearson's[5] value of 0 873 for TlSe Free elements or TlCl were not observed
Mercuric selenide (tiemannite) HgSe	(A) 2 066 g Hg in 10 ml hot 1 1 HNO_3 (B) 0 814 g Se in 9 ml 2 1 HNO_3	15 g N_2H_4 2HCl 150 ml H_2O 50 ml NH_4OH	98 7% HgSe was the only detectable crystalline matter present The crystallite size was quite small (0 1 μ)
Nickel selenide NiSe	(A) 0 5902 g Ni in 4 ml 1 1 HNO_3 (B) 0 7930 g Se in 4 5 ml 2 1 HNO_3	5 g N_2H_4 2HCl 1 g tartaric acid 100 ml H_2O 35 ml NH_4OH†	100 0% NiSe was the only detectable crystalline component The crystallite size was extremely small in the range of a few hundred angstroms

---

(3) J V Smith, *Index to the X-ray Powder Data File ASTM*, Philadelphia, Penna (1959)

(4) M Hansen *Constitution of Binary Alloys* McGraw-Hill, New York (1958)

(5) W B Pearson *A Handbook of Lattice Spacings and Structures of Metals and Alloys* Pergamon Press, New York (1958)

TABLE 1 (*continued*)

Compound and formula	g A and B in ml solvent	Composition of reducing solution	% Yield and X-ray diffraction analysis
Copper selenide $Cu_{2-x}Se$, where $x \sim 0 2$	(A) 1 1437 g Cu in 8 ml 1 1 HNO_3 (B) 0 7896 g Se in 6 ml 2 1 HNO_3	5 g N_2H_4 2HCl 125 ml H_2O 50 ml NH_4OH	101 4% The only component observed was $Cu_{2-x}Se$, where $x \sim 0 2$ No free elements were detected
Copper silver selenide (eucairite) CuAgSe	(A) 0 6354 g Cu in 6 ml 1 1 HNO_3 (B) *1 6989 g $AgNO_3$ in 10 ml H_2O, then 20 ml NH_4OH (C) 0 7896 g Se in 6 ml 2 1 HNO_3*	10 g N_2H_4 2HCl 150 ml H_2O 40 ml NH_4OH	100 2% The major lines of the sample could be indexed simple tetragonal, with *c/a* 1 543, in agreement with data in *Structure Reports* for eucairite

---

* The Hg and Se solutions were mixed, without using rinse water, by pouring back and forth to avoid hydrolysis Some of the hot reducing liquor was used to rinse the beakers after the addition, and was followed by the water rinses

† NH_4OH additions of 17 ml each were made at 15, 30 45, 75 and 105 min from start of boiling in the NiSe *preparation (to prevent hydrolysis of unreacted* Ni *salts due to loss of NH_3)* The boiling period was for 2 5 hr instead of the usual 1 5 hr

In some cases, the component elements could be dissolved together in the same beaker, but usually faster solution was obtained in separate beakers

Where dilute acids or bases were used, as in 2 1 HNO_3 the volume of active component is given first, and that of H_2O second

Experiments X-ray powder patterns were obtained using a General Electric XRD-3 Diffractometer equipped with CuK_α radiation filtered through nickel foil (λ 1 5418 Å) The instrument settings were X-ray tube current, 15 mAp, X-ray tube potential 50 kV defining slit 1 Soller slit, wide detector slit, 0 2 , target-to-beam angle, 4 , scanning rate 2 /min recorder range, 2 time constant, B, and recorder chart speed, 0 4 in / min

DISCUSSION

It was considered important to add the mixed metals solution to the reducing agent, rather than in the reverse sequence, to avoid contamination of the desired product with possible insoluble hydrolysis products

BENZING *et al* ventured that, since selenium is soluble to some extent in hydrazine the following reaction takes place

$$6N_2H_4 + 3H_2O + (2x + 1)Se \rightleftarrows 6N_2H_5^{+} \quad 2Se_x^{2-} \quad SeO_3^{2-}$$

In this case, the Se_x^{2-} would presumably react with the metal ion or free metal, if already reduced, to form the metal selenide The SeO_3^{2-} would be reduced to free Se to make the reaction go to the right The formation of an intermediate soluble selenide ion with hydrazine seems to be reasonable, since one can prepare CdSe and TlSe whereas Cd^{2+} and Tl^{+} alone are not reduced to the free metal by hydrazine However, it is noteworthy that the writer has succeeded in preparing Ag_2Se and HgSe using as a reducing agent acidified solutions of ammonium sulfite, and also Ag_2Se

using ammoniacal dextrose or hydroxylamine solutions, none of which contained any hydrazine. Each of these was made in a manner analogous to that described in Table 1, obtained in 99–100 per cent yields, and verified by X-ray diffraction analysis. Further, the writer's earlier publication$^{(1)}$ has shown that many types of compounds, including intermetallics, antimonides, arsenides and tellurides, can be made with this same general method, sometimes in acidic H_3PO_2 solutions, sometimes in alkaline hydrazine. It was suggested there that reaction appears to take place between the reduced elements themselves while in an intimately mixed, finely-divided and highly active state. It would seem that this type of reaction predominates when acidic sulphite, H_3PO_2 or ammoniacal dextrose is used in preparing selenides, and that it might figure also when hydrazine is used, in competition with the intermediate soluble selenide reaction.

Acknowledgment—Thanks are extended to Messrs. J. H. DICKESS in preparations and R. FERGUSON in X-ray diffraction analysis.

J. Inorg. Nucl. Chem. 1963, Vol. 25, pp. 79 to 86. Pergamon Press Ltd. Printed in Northern Ireland

STUDIES ON ARSENIC TETROXIDE—I

THE INTERACTION OF ARSENIC TRIOXIDE AND ARSENIC PENTOXIDE

L. H. Long and J. F. Sackman*
Department of Chemistry, University of Exeter

(*Received* 10 *November* 1961)

Abstract—Although mixtures of the anhydrous trioxide and pentoxide of arsenic react chemically on heating, contrary to statements in the literature it is not feasible to prepare even an approximately pure sample of arsenic tetroxide by this method. The reaction has been followed on the thermal balance at 350, 400 and 430°C, and although the composition of the product varied with the temperature, it was invariably grossly deficient of trivalent arsenic. This deficiency could not be remedied by using an excess of arsenic trioxide and subliming off the excess, by reheating with further quantities of trioxide, or by preheating in a sealed tube.

In the presence of an adequate quantity of water, however, almost pure arsenic tetroxide can be prepared from an equimolecular mixture of trioxide and pentoxide. Sufficient water to dissolve the oxides at 100–110°C is required, and evaporation of the solution first gives a hydrate $6As_2O_4.5H_2O$ stable at 110°C. On stronger heating the water is driven off to leave As_2O_4, stable at 400°C. Use of an excess of trioxide is not recommended, as the product prepared by this method can hold an excess of trioxide tenaciously, even at 400°C, although it is slowly given up at 500°C. The separate chemical identity of As_2O_4 is confirmed by X-ray studies. It is probably incorrect to regard the compound as arsenious arsenate $As^{III}[As^{V}O_4]$.

These studies were originally undertaken in order to gain a clearer understanding concerning the nature of the products of combustion of trimethylarsine,(1) the heat of formation of which it was desired to determine. When burnt in oxygen under pressure, this compound, like elementary arsenic, gives a mixture of oxides which analyses for tri- and pentavalent arsenic. However, even if both As_2O_3 and As_2O_5 are originally formed, it seemed likely that under the prevailing experimental conditions they would interact to give As_2O_4, the existence of which has been reported. But since the tetroxide has not been very well characterized and much of the data published concerning it are inconsistent, a reinvestigation of its preparation and some of its more important properties, including its heat of formation, became necessary.

This investigation falls naturally into three parts. The present paper deals with attempts to prepare As_2O_4 from As_2O_3 and As_2O_5. Investigations of the products of combustion of arsenic in a bomb under pressure will be reported in Part II, while the results of thermochemical studies on some of the products described in the first two parts will be deferred to Part III.

Although As_2O_4 is cited by many standard textbooks in inorganic chemistry, no systematic investigation of its properties has been reported and there are only two accounts of its preparation. In the first(2) of these Herbst claimed to have prepared the tetroxide by heating mixtures of As_2O_3 and As_2O_5 in varying proportions at 350°C. In the second,(3) Ghiron and Mangili found that they could not repeat some of Herbst's work, but claimed to have prepared the tetroxide by heating As_2O_3 with arsenic acid. Clearly therefore, the state of knowledge concerning this compound was to be regarded as far from satisfactory.

---

* Present address, A.W.R.E., Aldermaston, Berks.

(1) L. H. Long and J. F. Sackman, *Trans. Faraday Soc.* **52,** 1201 (1956).

(2) H. Herbst, *Diss. Bern* **30,** 16 (1894).

(3) D. Ghiron and G. Mangili, *Gazzetta* **65,** 1244 (1935).

In studying the effect of temperature, HERBST found that on heating an equimolecular mixture of the trioxide and pentoxide of arsenic at 350°C no loss in weight occurred, although the trioxide alone is appreciably volatile at this temperature. He attributed this behaviour to the formation of the tetroxide. HERBST also stated that, at 350°C, mixtures containing an excess of trioxide or of pentoxide lost trioxide or oxygen respectively until the ratio of oxides was equimolecular. The last statement implies that arsenic pentoxide is converted to the tetroxide on heating. In contrast to this, GUÉRIN and BOULITROP assume(4) that the pentoxide is in simple equilibrium with the trioxide and oxygen without the interposition of the tetroxide. Probably neither view is correct however, as is indicated both by the present work and by that(5) of WEIDENBACH who found the product of decomposition of As_2O_5 at 800–1200°C to consist of an oxide of formula $2As_2O_3 \cdot As_2O_5$.

On the other hand according to GHIRON and MANGILI,(3) the most stable oxide at 400°C is the tetroxide, and this can be prepared by heating mixtures of the trioxide and arsenic acid ($As_2O_5 \cdot nH_2O$) in the theoretical ratio for several hours, when the ratio remains constant at that corresponding to the tetroxide. The same product is also stated to be obtained on prolonged heating, at the same temperature, of a mixture of the same compounds but with an As(III):As(V) ratio of two, the excess of trioxide presumably subliming off. Above 400°C, according to these investigators, the tetroxide starts to decompose, and at 600°C only pentoxide remains (in stark contrast to HERBST's statement that the pentoxide is converted to the tetroxide). GHIRON and MANGILI claim further that X-ray studies show a definite compound, and conclude from comparison with similar investigations on arsenic phosphate ($AsPO_4$) that arsenic tetroxide is arsenious arsenate $As(III)As(V)O_4$.

The same investigators(3) also reinvestigated the work of HERBST, and report that a compound identical with that prepared by their method results from heating an equimolecular mixture of the trioxide and the pentoxide, and also from heating a mixture containing an excess of trioxide at 400–500°C until the excess sublimes away. They were unable to prepare the same compound by heating the pentoxide. A mixture of As_2O_3 and $As_2O_5 \cdot nH_2O$ in the ratio 1:2 when heated at 400°C for 8 hr had an As(III):As(V) ratio of 0.56. A further 4 hr at 500°C reduced this ratio to 0.46, and finally at 600°C no As(III) remained. It does not, however, necessarily follow from this that the pentoxide is indefinitely stable at this temperature, since the more recent work of GUÉRIN and BOULITROP(4) reveals that the dissociation pressure of the pentoxide is already 1 mm at 500°C, although no oxygen was detectable below 450°C.

It can be seen that the results of the investigations by HERBST and by GHIRON and MANGILI are not completely in harmony, the most significant point of difference being the failure by the latter authors to obtain complete conversion to the tetroxide of a mixture originally containing an excess of pentoxide, as HERBST claims to have done. It is also not clear whether GHIRON and MANGILI support HERBST's contention, that on heating a mixture containing an excess of trioxide to an appropriate temperature only the excess sublimes. They report the formation of the tetroxide on heating until the excess sublimed, but apparently did not continue heating beyond that point.

---

(4) H. GUÉRIN and R. BOULITROP, *C. R. Acad. Sci. Paris* **236**, 83 (1953).

(5) E. WEIDENBACH, *Diss.*, *Berlin* (1915).

It has also been claimed(6) that As_2O_4 is formed when As_2O_3 is heated at 400–480 °C under 150–180 atm of oxygen, and when ceric salts act on a solution of As_2O_3,(7) according to the equation

$$Ce^{4+} + AsO_2 \rightarrow Ce^{3+} + AsO_2$$

However, later work shows(8) that the latter reaction proceeds until all the arsenic is in the pentavalent state.

EXPERIMENTAL AND DISCUSSION

1. *Experiments with dry mixtures of arsenic trioxide and arsenic pentoxide*

In these experiments, use was made of the fact that As_2O_4 and As_2O_5 are non-volatile over the temperature range 350–430 °C, while As_2O_3 (which reaches a sublimation pressure of 1 atm at 460 °C) is sufficiently volatile to sublime away completely within a few hours. Accordingly, to remove excess As_2O_3 it was merely necessary to continue heating until there was no further loss in weight. In all cases, the As_2O_3 and As_2O_5 were intimately mixed and then heated under the conditions described. The heated mixtures were ground and portions dissolved in dilute alkali for subsequent analysis for trivalent and pentavalent arsenic, the former by titration against standard KIO_3, the latter by titrating the iodine liberated from acidified KI solution.

1.1. *Action of heat on mixtures containing an excess of trioxide.* A well-ground mixture (20 g) with the trioxide and pentoxide in the molecular ratio 1.271 : 1 and contained in a silica crucible fitted with a lid was heated in a furnace at 400 °C for 5 hr. The weight was recorded every hour and the rate of loss of weight was observed to decrease with time. When heating was resumed for the last time the temperature of the furnace was inadvertently raised from 400 to 700 °C over a period of 30 min after which time the oxides were molten. However, the resultant loss in weight was not appreciably greater than that for the last hour at 400 °C. Analysis corresponded to an As(III) : As(V) ratio of 0.928. This showed that more than the excess of trioxide had sublimed after 30 min at 700 °C.

The experiment was repeated with a similar mixture (16 g) except that it was heated at 350 to 400 °C for 14 hr, the weight being recorded at intervals. After 5 hr the loss in weight per gramme of mixture was similar to that observed in the previous experiment and the total loss corresponded approximately to the excess of trioxide. However, the loss in weight continued progressively after this time, although the rate of loss diminished steadily and in the last hour was only 0.02 g in 12 g of mixture. Analysis gave an As(III) : As(V) ratio of 0.753, thus indicating, as did the previous experiment, that the preparation by the method of HERBST is not as simple as that investigator states.

1.2. *Action of heat on equimolecular mixtures.* These and subsequent experiments were carried out on a thermal balance in order to eliminate intermittent periods of cooling, to follow the change in weight more rapidly and easily, and to determine whether this provided any indication of the chemical processes involved on heating mixtures of oxides.

Three samples (7.75 g each) of the equimolecular mixture were heated in pyrex test-tubes on a thermal balance at 350, 400 and 430 °C respectively. The losses in weight are plotted against time in Fig. 1. It can be seen that in the experiments carried out at 400 and 430 °C the losses in weight ceased after 21 and 13 hr respectively, but that the sample maintained at 350 °C was still losing weight when heating was discontinued after 33 hours. Analyses gave As(III) : As(V) ratios of 0.605, 0.712 and 0.721 at 350, 400 and 430 °C respectively.

These results show that a considerable loss of trioxide occurred at all temperatures, but that at 400 and 430 °C some reaction had clearly occurred to prevent the remainder of the trioxide from subliming. As the explanation of the results was possibly that the reaction is too slow to permit the two oxides to complete reaction to the tetroxide before some of the trioxide volatilized away, it was decided to repeat the experiments with mixtures containing an excess of trioxide after preheating them over prolonged periods in sealed tubes. Since an excess of trioxide would be present the whole time, it was reasoned that all the pentoxide would have a chance to react, so that on subsequent heating in an open tube only the excess of trioxide would sublime.

C. Matignon and J. A. Lecanu, *C. R. Acad. Sci., Paris* **170**, 941 (1920).

V. F. Stefanovskiĭ and M. S. Gaukhman, *J. Gen. Chem. U.S.S.R.* **11**, 970 (1941).

J. W. Moore and R. C. Anderson, *J. Amer. Chem. Soc.* **66**, 1476 (1944).

1 3 *Action of heat on mixtures containing an excess of trioxide and preheated in sealed tubes* Three samples (10 g each) of a mixture with the trioxide and the pentoxide in the molecular ratio 1 204 1 were heated in sealed tubes at 350 400 and 430 C for 48, 24 and 24 hr respectively The mixtures, which in the first two cases had sintered and in the last had fused, were ground and heated in Pyrex test-tubes on the thermal balance at the same respective temperatures The losses in weight against

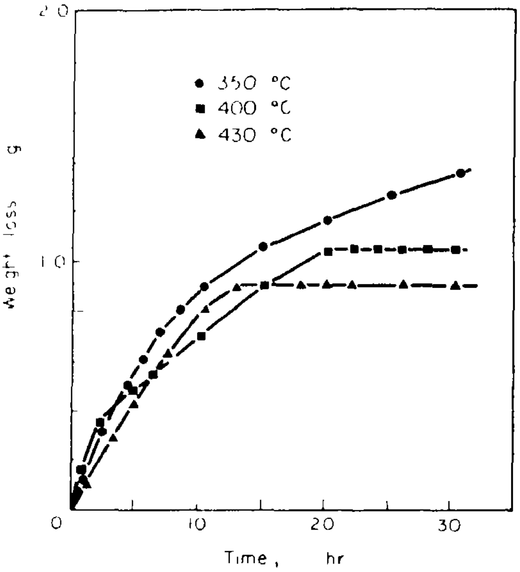


FIG. 1 —The loss in weight with time of dry equimolecular mixtures of As_2O_3 and As_2O_5 at 350 400 and 430 C respectively [Experiment (1 2)]

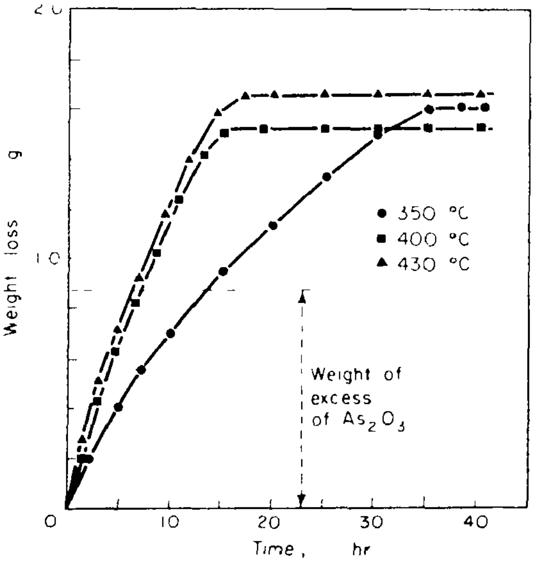


FIG. 2 The loss in weight with time at 350, 400 and 430 C respectively of preheated dry mixtures of As_2O_3 and As_2O_5, containing an excess of As_2O_3 [Experiment (1 3)]

time shown in Fig 2 are seen to be much in excess of those expected, although in these experiment they all became negligible after a certain time It may be of interest to note that whereas in Experiment (1 2) the total loss in weight was greatest in the case of the sample heated at 350 C and least i the case of that heated at 430 C, this order was not observed in the present instance, where the As(III) As(V) ratios were 0 797, 0 811 and 0 781 at 350, 400 and 430 C respectively

Although preheating has some effect, complete reaction is not achieved Indeed, viewed as a possible way of preparing the tetroxide, the experiments, especially in the cases of samples at 400 430°C, exhibit very little improvement on the previous series

To ascertain that this was not due to insufficient preheating, a mixture (9 g) containing the trioxide in a molecular excess of 1 3 1 was preheated in a sealed tube at 400 C for 112 hr After crushing and reheating in the usual way, the final As(III) As(V) ratio was 0 814, almost exactly the same as before

The failure of earlier experiments does not, therefore, seem to be merely a question of the speed of reaction Nor does it seem to be a question of the intimacy of mixing since the sample heated at 430°C in a sealed tube fused but still failed to react to completion In view of these unsuccessful attempts to prepare pure arsenic tetroxide directly the next experiment undertaken was an attempt to introduce arsenic trioxide into As(III)-deficient products of the type already obtained

1 4 *Action of heat on a preheated mixture of oxides admixed with additional trioxide* An equimolecular mixture (8 g) of the trioxide and the pentoxide was heated in a sealed tube at 400 C for 48 hr then ground and reheated on the thermal balance in the usual way The loss in weight against time curve is shown in Fig 3 On comparison with the curve in Fig 1 obtained in a similar experiment with no preheating it is again seen that the loss in weight is somewhat less The resulting solid was ground with an amount of trioxide approximately equal to the loss in weight (~0 6 g) and the new mixture heated on the thermal balance at 400 C The rate of loss and total loss in weight are seen from the curve, also given in Fig 3, to be identical with the previous run showing that no further reaction occurred The procedure was repeated, but an approximately 1 g excess of trioxide was added (total ~1 6 g) and the mixture heated in a sealed tube at 400 C for 38 hr before heating on the thermal balance The plot of loss in weight against time is also given in Fig 3 and the total loss in weight is seen to exceed 1 5 g showing that less than 0 1 g of the trioxide added in the last operation was taken up Analysis of the final product gave the As(III) As(V) ratio 0 810 which is almost identical with that for the sample preheated in a sealed tube at 400 C in Experiment (1 3) This indicates that the excess of trioxide used in that case had little effect on the composition of the product

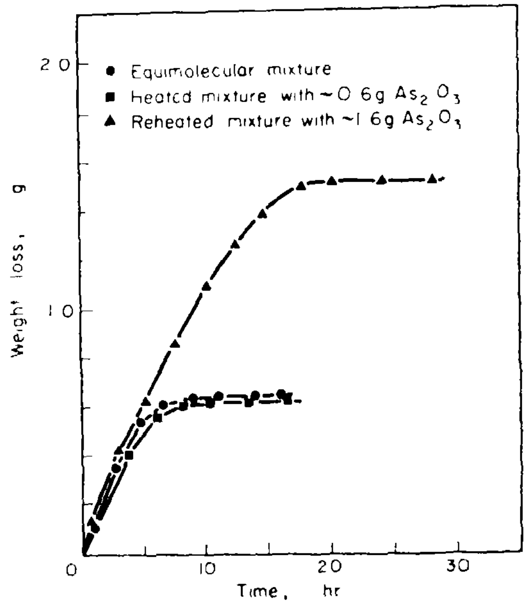


Fig 3—The loss in weight with time at 400 C of a preheated dry equimolecular mixture of As_2O_3 and As_2O_5 after admixture with further As_2O_3 [Experiment (1 4)]

Conclusions If GHIRON and MANGILI's statement that arsenic tetroxide is stable at 400 C is true and later results in the present study support this—it seems on the basis of the foregoing experiments not to be feasible to prepare a sample of pure arsenic tetroxide by heating either an equimolecular mixture of the trioxide and the pentoxide or a mixture with any other ratio at about 400 C Perhaps the most significant point emerging from these results is that whereas reaction definitely occurs the final product in every case (where heating was continued until the rate of loss in weight became negligible) contained between 41 6 and 44 9 per cent of its arsenic in the trivalent state, depending to some extent on the temperature The results are clearly at variance with those reported by HERBST

2 *Experiments with wet mixtures of arsenic trioxide and arsenic pentoxide*

Further attempts to prepare the pure tetroxide were carried out by modifications of the method of Ghiron and Mangili that is in effect using arsenic acid $As_2O_5 \cdot nH_2O$ as the starting material in place of the anhydride As_2O_5

2 1 *Action of heat on an equimolecular mixture preheated in a sealed tube* An equimolecular mixture (8 g) was made into a paste with the quantity of water (1 ml) required to convert the pentoxide present into the hypothetical ortho-arsenic acid H_3AsO_4 In order to provide opportunity for this transformation to complete itself the paste was heated in a sealed tube at 110 C for 19 hr before it was heated on the thermal balance in the usual way at 400 C

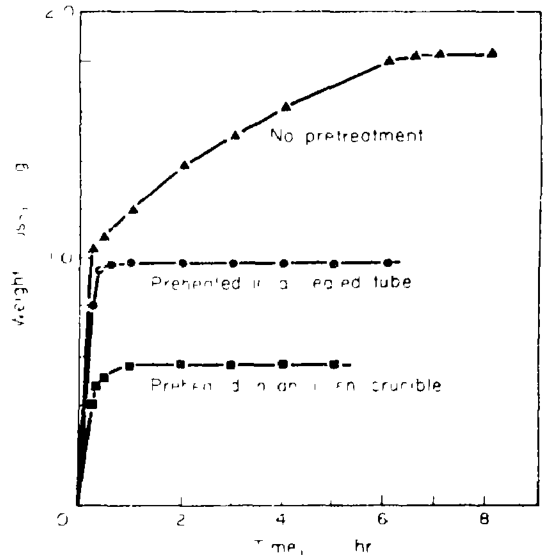


FIG 4 -The loss in weight with time of wet equimolecular mixtures of As_2O_3 and As_2O_5 at 400 C [Experiments (2 1), (2 2) and (2 3)]

The loss in weight plotted against time is shown in Fig 4 The very rapid initial loss in weight corresponded to the quantity of water present As the final product had the As(III) As(V) ratio 0 945, the greater proximity of this ratio to that required for the tetroxide and the shape of the loss in weight curve make it seem probable that in this experiment the tetroxide was formed during the preheating To check this point the experiment was repeated omitting the preliminary heating in a sealed tube

2 2 ***Action of heat on an equimolecular mixture without preheating*** An equimolecular mixture (8 was mixed with water (1 ml) and the paste heated (without preheating at 110 C) on the thermal balan

at 400 C The loss in weight curve, also given in Fig 4, is seen to be very different from the first curve (Experiment (2 1)), as was the composition of the final product, which had an As(III) As(V) ratio of 0 780

It thus seems that initial heating in the presence of water is a prerequisite for a high conversion to arsenic tetroxide It is of interest to note that (a) the shape of the curve after removal of the water, (b) the time for the rate of loss in weight to become negligible and (c) the analysis of the final product, all correspond closely to those observed for the equimolecular mixture of the dry oxides that was heated in a sealed tube for 48 hours at 400°C (Experiment (1 4) and Fig 3) A further experiment was carried out to determine whether the preheating with water, now shown to be necessary, needed to be in a sealed tube

2 3 *Action of heat on an equimolecular mixture preheated in an open crucible* In order to keep the oxides in contact with water for a reasonable time, a larger amount of water than that required to convert the pentoxide to ortho-arsenic acid was used An equimolecular mixture of oxides (8 g) was mixed with water (~8 ml) and heated at about 110 C in an open crucible The amount of water was initially sufficient to dissolve the oxides completely When the crucible and contents had reached constant weight, part of the resultant solid was anlysed and the rest ground and heated on the thermal balance at 400°C in the usual way

The loss-in-weight curve is also shown in Fig 4 and is seen to be identical in form to that from Experiment (2 1) The As(III) As(V) ratio of the final product was 0 982 The latter figure corresponds to 49 5 per cent of the arsenic present being in the trivalent state, which is sufficiently close to the 50 per cent required for the tetroxide to show that heating in a sealed tube is not necessary

Experiments (2 1), (2 2) and (2 3), taken together, appear to indicate that the tetroxide possibly first in a hydrated form is preferably formed in solution However, it is probably wrong to suggest that arsenic tetroxide is really arsenious arsenate As(III)[As(V)O$_4$], since the mixing of arsenious and arsenic acids in solution is not accompanied by any measurable heat effect that can be attributed to a heat of neutralisation,(11) moreover the rate of solution of arsenic tetroxide in water is low Accordingly, the oxygen in the compound is probably linked to the trivalent as well as the pentavalent arsenic It should however be remarked that analysis of the wet mixtures after drying at 110°C but before heating on the thermal balance always revealed that water was present to the extent of 11 6 per cent of the weight of the pentoxide originally present, and since separate experiments also showed that arsenic pentoxide when mixed with water and heated to constant weight at 110°C retained 11 56 per cent of its weight of water (corresponding to the known hydrate $3As_2O_5\ 5H_2O$(9 10) it is tempting to suppose that the mixtures of oxides after drying at 110 C and before heating at 400 C consist of nothing other than a mixture (or loose association) of the trioxide and the hydrated pentoxide $3As_2O_5\ 5H_2O$ This view is however incorrect and that the product is rather to be regarded as a hydrated form of the tetroxide of formula $As_2O_4\ 5H_2O$ is clearly revealed by X-ray powder photographs which show the same diffraction lines as anhydrous As_2O_4, and none of those associated with As_2O_3 or As_2O_5 (cf Part II, Plate I) Accordingly As_2O_4 is definitely already present after drying at 110 C, and the similarity in the amounts of water retained at this stage is coincidental The water is comparatively loosely held, apparently in spaces in the As_2O_4 lattice, since when it is driven off by stronger heating the diffraction lines

---

D Balareff *Z Anorg Chem* 71, 73 (1911)

A W Menzies and P D Potter, *J Amer Chem Soc* 34, 1452 (1912) remain practically unchanged, confirming that there is no essential change in the lattice structure

Because the final products from the wet method still exhibited a slight deficiency in trivalent arsenic similar experiments were carried out on mixtures containing an excess of trioxide in order to ascertain whether it is possible to obtain a pure sample of arsenic tetroxide by this modification in technique

2 4 *Action of heat on mixtures containing an excess of trioxide preheated in a sealed tube* A mixture (8 6 g) containing the trioxide and the pentoxide in the molecular ratio 1 294 1 was mixed with water (1 5 ml) and heated in a sealed tube at 110 C for 48 hr Although shown not to be necessary, the preheating was carried out in a sealed tube in order to provide conditions that were more reproducible experimentally The mixture was subsequently ground and reheated at 400 C on the thermal balance The rate of loss in weight became negligible after 6 hr but after 18 hr heating the As(III) As(V) ratio of the product was still 1 107 A further 32 hr heating at 400 C resulted in only a very small loss in weight amounting to only 0 002 g out of 7 5 g in the last 10 hr Analysis then showed a molecular ratio of 1 043 1 For the next 24 hr the temperature was raised to 450 500 C but an excess of trioxide still remained and a further 24 hr at 500 C were needed to remove this excess During the last period of heating the rate of loss in weight did not become negligible and more than the excess of trioxide sublimed A final analysis gave the As(III) As(V) ratio 0 990 corresponding to 49 75 per cent of the arsenic in the trivalent state

It is difficult to understand why all the excess of trioxide did not sublime at 400°C In order to determine whether this might be due to the formation of a small amount of an intermediate oxide containing the trioxide in more than an equimolecular ratio, an experiment was carried out with a mixture containing a large excess of the trioxide, so that any such compound would have a greater chance of being formed

The mixture used contained the trioxide and the pentoxide in the molecular ratio of 3 421 1 Because of the large excess of the trioxide, over 40 hr heating at 400 C were required before the rate of loss in weight became negligible, but analysis then showed an As(III) As(V) ratio of 1 143 An hour at 500 C changed this ratio to 1 068 and a further 24 hr at the same temperature during which time the weight continued to decrease albeit slowly, resulted in a ratio of 0 978

The fact that with such a large excess of the trioxide, most of the excess sublimed at 400 C, suggests that the explanations of the retention of moderate quantities at this temperature does not lie in the formation of a different intermediate oxide richer in trivalent arsenic

At least two possible explanations for the tendency to retain trioxide suggest themselves The first is that the trioxide is trapped in small pockets during the sintering that always occurred in these experiments, and this would greatly retard its rate of sublimation The second is that arsenic tetroxide may not be a stoicheiometric compound As both the trioxide and the pentoxide readily form glasses, it is not unlikely that the tetroxide which may be assumed to contain both tri- and pentavalent arsenic, would show a similar tendency The lattice so formed, although possibly most stable with the composition As_2O_4, might be slightly deformed to accommodate an excess of either the trioxide or the pentoxide This could explain the compositions observed on both sides of stoicheiometric proportions

Conclusions The results of this series of experiments indicate that arsenic tetroxide is readily formed by heating an equimolecular mixture of the trioxide and the pentoxide first with water at 110 C and then at 400°C It seems possible that the formation takes place during the initial heating at 110°C The results of Experiment (2 4) at 400–500 C support Giiron and Mangili's conclusion that the tetroxide is unstable above about 400°C

J. Inorg. Nucl. Chem. 1963. Vol. 25. pp. 89 to 91. Pergamon Press Ltd. Printed in Northern Ireland

STUDIES ON ARSENIC TETROXIDE—II

THE COMBUSTION OF ARSENIC IN OXYGEN UNDER PRESSURE

L. H. LONG and J. F. SACKMAN*
Department of Chemistry, University of Exeter

(*Received* 10 *November* 1961)

Abstract—The combustion of arsenic under anhydrous conditions in a bomb under 20–30 atm of oxygen gave a mixture of oxides, partly sublimed and partly in a glassy state, with the As^{III}:As^{V} ratio always much in excess of unity. The products were studied by (a) analysis, (b) behaviour on partial extraction with water, (c) thermal behaviour on dissolution, and (d) X-ray powder photographs. The glassy products behaved as As_2O_3–As_2O_4 mixtures with no evidence for uncombined As_2O_5. In the sublimate, however, most of the As(V) was initially in the form of uncombined As_2O_5 which only combined to As_2O_4 on exposure to moisture, while the As(III) was mostly initially present in a new and highly energy-rich modification of As_2O_3 with a solubility greater than thirty times as great as that for normal As_2O_3 (to which it slowly reverted in contact with atmospheric moisture). Combustion of arsenic metal in a bomb calorimeter in the absence of water is therefore an unsuitable method for determining the heats of formation of the oxides of arsenic.

As_2O_4 is a definite compound and gives characteristic X-ray diffraction lines. The X-ray studies furnished no evidence for the formation of any intermediate oxide of arsenic other than As_2O_4 under the conditions investigated in the present work.

To date, only one investigation on the combustion of elementary arsenic in oxygen under pressure has been reported in the literature, this[1] being due to de PASSILLE, who burnt arsenic in a bomb in order to determine its heat of combustion. He reported that the main product of combustion was the trioxide, but that the proportion of pentoxide increased with increasing pressure of oxygen, reaching 27.7 per cent by weight (corresponding to 24.8 per cent of the arsenic in the pentavalent state) at 40 atm initial pressure. He also reported that, after each combustion experiment, the walls of the bomb were observed to be covered with a thick layer of crystalline trioxide, while the crucible retained a quantity of arsenic tetroxide as a fused opaque mass. No evidence was advanced to support the assertion that this opaque substance was in fact As_2O_4. Accordingly, a more detailed investigation of the products of combustion appeared desirable.

MATERIALS AND PROCEDURE

The elementary arsenic used in this work was sublimed material supplied in powder form by British Drug Houses. All soluble impurities were removed by boiling with moderately concentrated hydrochloric acid, followed by filtering, successively washing with water, alcohol and ether, and finally drying in a vacuum desiccator. Combustions were performed with 10 g quantities and were carried out in a silica crucible supported inside a stainless-steel bomb so as not to make contact with the base of the bomb. The bomb was previously filled with dry oxygen under a pressure of 20, 25 or 30 atm. Ignition was effected by electrically firing a short length of fine iron wire attached to a small piece of magnesium ribbon as a fuse.

After combustion the products were analysed for tri- and pentavalent arsenic as already described[2] in Part I.

---

* Present address: A.W.R.E., Aldermaston, Berks.

[1] A. de PASSILLE, *Ann. Chim.*, **5**, 83 (1936).

[2] L. H. LONG and J. F. SACKMAN, *J. Inorg. Nucl. Chem.*, **25**, 79 (1963).

RESULTS AND DISCUSSION

In all cases, combustion of the arsenic produced a voluminous, white, powdery sublimate which collected on the floor of the bomb, while a glassy mass remained in the crucible. Analyses of the sublimates and the glasses are given separately for comparison in Table I, each figure being the average for the products of two or three combustions.

TABLE 1.—ANALYSES FOR THE SUBLIMATES AND GLASSES REMAINING AFTER THE COMBUSTION OF ELEMENTARY ARSENIC

Initial pressure of oxygen (atm)	Sublimate % arsenic as		Glass % arsenic as	
	As(III)	As(V)	As(III)	As(V)
20	84.88	15.12	79.38	20.62
25	79.23	20.77	74.08	25.92
30	75.15	24.85	70.13	29.87

It is doubtful whether the higher percentage of As(III) in the sublimed material in each case is very significant, since it may well be explained by the greater volatility of the trioxide. It is to be noted that whereas the appearance of the products after combustion was similar to that described[1] by de PASSILLE, the composition found for the glass is at variance with that author's statements, being everywhere far from that required by As_2O_4. It was noted that the glass started to devitrify and became opaque on standing, and also that it was slowly soluble in alkali. As the main product was the sublimate, the glass was not further examined, except that an X-ray powder photograph was taken of one specimen of the mechanically powdered glass for comparison with those given by the sublimates (see later).

In each case, however, the sublimate showed certain striking properties which differentiated it from the normal oxides of arsenic. As can be seen from Table 1, at all pressures of oxygen a large excess of the trioxide over the pentoxide was present, the molecular ratios being 5.61, 3.81, and 3.03 at 20, 25 and 30 atm respectively. There is thus more than sufficient trioxide to combine with all the pentoxide present to give the tetroxide.

Behaviour of products on limited extraction with water

A possible way of determining whether in fact any tetroxide had been formed was to subject the sublimates to extractions with water of limited duration and determine the respective amounts of trivalent and pentavalent arsenic passing into solution by analysis. From a knowledge of the behaviours of the trioxide, tetroxide and pentoxide respectively towards water, it was expected that some conclusions could be drawn regarding the state of the oxides produced in the bomb. Use was made of the following experimental facts regarding the behaviour of the three known oxides towards water:

(a) arsenic trioxide dissolves only very slowly in water, even on vigorous stirring—of 4.524 g of the finely crystalline, sublimed oxide stirred with 150 ml of water at 18°C for 30 min only 0.0379 g (0.84 per cent) dissolved, and of 5.724 g of the oxide stirred with a similar quantity of water for 60 min only 0.0686 g (1.20 per cent) dissolved (it was subsequently shown that the rate of dissolution in a solution of arsenic acid is likewise very slow);

(b) arsenic pentoxide is comparatively slow in dissolving in water, but does so more rapidly than the trioxide—of 1.009 g of the finely powdered anhydrous oxide stirred with 250 ml of water at 18°C just over half dissolved in 15 min and all dissolved within 2 hr;

(c) arsenic tetroxide dissolves more rapidly than either the trioxide or the pentoxide 1 210 g of the finely powdered tetroxide (prepared by heating equimolecular quantities of the trioxide and pentoxide with water at 110 and subsequent drying at 400 C) on stirring with 250 ml of water at 18 C dissolved completely within 30 min

If it can now be assumed in the first instance that no intermediate oxide other than the tetroxide results from any compound-formation between the trioxide and pentoxide formed in the bomb, the products can be considered to be constituted in one of three possible ways

(i) As_2O_3 and As_2O_5, if no compound-formation occurs,

(ii) As_2O_3, As_2O_4, and As_2O_5, if some As_2O_5 combines,

(iii) As_2O_3 and As_2O_4, if all the As_2O_5 combines

On the basis of the experimental facts given above, rapid partial extraction with water of these combinations should dissolve

(i) mainly As_2O_5 with a little As_2O_3,

(ii) a mixture of As_2O_4 and As_2O_5 with a little As_2O_3,

(iii) mainly As_2O_4 with a little As_2O_3

The As(III) As(V) ratio in the resultant solution would accordingly show a marked difference in the three cases, being namely 1 for case (i), ~1 for case (ii) and 1 for case (iii)

The bomb products to be tested in this way were protected from atmospheric moisture by storing in a vacuum desiccator A known quantity of each solid was placed in a sintered glass crucible attached to a filter pump and covered with a measured quantity of cold water, which was sucked through the crucible after a predetermined time of contact The filtrate was then analysed in the usual way for tri- and pentavalent arsenic The results for a number of different products are recorded in Table 2 The figures in colum 5 represent the times of contact with water to the completion of filtration The oxides formed with 20, 25, and 30 atmospheres of oxygen are designated A B and C respectively Experiments 3a 6a and 7a refer to a second extraction of the residues from experiments 3, 6, and 7 respectively

The most striking feature of these results which are quite unlike anything expected, is the extremely large amount of solid dissolved in such a small volume of water in such a short time and, in particular, the large quantity of trioxide dissolving in all the first extractions Thus, for example in experiment 7 the amount of trivalent arsenic dissolving is equivalent to 0 32 g of As_2O_3 in 5 ml, a concentration corresponding to a solubility more than thirty times that of normal As_2O_3 moreover the rate of solution is several thousand times that noted for ordinary As_2O_3 These observations clearly indicate the formation of an oxide (or oxides) of a type not previously encountered

The unexpected ratios found in the last column of Table 2 though instructive do not of themselves lead to a straightforward conclusion regarding any intermediate oxide Perhaps the most consistent feature is that, for each of the oxides A B and C considered separately, the shorter the time of the first extraction the higher the relative proportion of As(III) going into solution, which would not be expected of ordinary As_2O_3 As_2O_5 mixtures On the other hand long extraction times (Experiment 1) or subsequent extractions (Experiments 6a and 7a) gave ratios below one revealing that not all the pentavalent arsenic is combined in the form of tetroxide Since the analyses reported in Table 1 show that there is always considerably more than enough trioxide to combine with all the pentoxide present, the evidence now presented is that all or part of the uncombined As_2O_3 in the bomb product exists in the form of an unusually active and soluble variety Although no such soluble variety seems to have been reported previously (the various known modifications having much lower solubilities),

TABLE 2.—ANALYSIS OF AQUEOUS EXTRACTS OF OXIDE SUBLIMATES PRODUCED BY THE COMBUSTION OF ARSENIC IN OXYGEN UNDER PRESSURE

Expt no.	Oxide sample	Weight (g)	Vol. of water (ml)	Time of contact (sec)	Arsenic dissolved As(III) (g)	Arsenic dissolved As(V) (g)	Ratio As(III)/As(V)
1	A	0.863	5	240	0.064	0.089	0.72
2	A	1.214	5	45	0.105	0.103	1.02
3	A	1.245	5	10	0.142	0.052	2.73
3a	A (residue)		5	60	0.190	0.078	2.44
4	B	0.894	10	120	0.229	0.123	1.86
5	B	1.484	10	45	0.415	0.205	2.02
6	B	0.884	5	30	0.204	0.100	2.04
6a	B (residue)		5	30	0.007	0.027	0.26
7	C	1.010	5	20	0.244	0.155	1.57
7a	C (residue)	—	5	75	0.020	0.048	0.42

it is readily conceivable that the special conditions prevailing in the bomb—where As_2O_3 vapour at a very high temperature is suddenly cooled—could give rise to an energy-rich modification.

Two further lines of evidence throw additional light on the situation. If the arsenic trioxide is in an energy-rich condition this should be revealed by the amount of heat liberated on dissolution in water. It was found calorimetrically that on adding the bomb products to water, a large amount of heat was evolved very rapidly. This (after allowing for some undissolved trioxide) was noted to be far in excess of that calculated for mixtures of equivalent quantities of As_2O_3 and As_2O_5, thus indicating the presence of an oxide strongly endothermic with respect to ordinary As_2O_3–As_2O_5 mixtures. Although this observation does not indicate the presence in the bomb sublimate of As_2O_4, which (as will be shown in Part III) is slightly exothermic with respect to As_2O_3–As_2O_5 mixtures, the possibility of its presence cannot be excluded, if only because of the large excess of As_2O_3 present.

The formation of this 'endothermic' or energy-rich variety of As_2O_3 in the bomb process clearly shows that attempts to determine the heat of formation of As_2O_3 by burning arsenic in a bomb are likely to be misleading. The energy-rich variety is unstable in contact with moisture, which rapidly causes it to revert to the normal modification. Thus exposure of the bomb sublimate to the atmosphere for only a short time greatly reduced its heat of solution.

The other additional evidence is supplied by the X-ray powder photographs reproduced in Plate 1, which were made because the problem could not be completely solved by chemical methods alone. Diffraction patterns 1 and 2 are included for reference, and refer to ordinary As_2O_3 and As_2O_5 respectively. The third exposure reproduces the pattern given by an almost pure sample of As_2O_4 prepared as in Part I by the wet method, and incorporates none of the lines given by As_2O_3 or As_2O_5. Clearly, therefore, As_2O_4 is a distinct compound with a characteristic pattern of its own; moreover, the absence of As_2O_3 or As_2O_5 lines confirms that the formula of the intermediate oxide is indeed As_2O_4. The fourth pattern is that given by hydrated arsenic tetroxide, $6As_2O \cdot 5H_2O$, and reveals no lines not given by anhydrous As_2O_4 itself. As expected, the products obtained in attempts to prepare As_2O_4 by the dry method (see Part 1) give, on account of the large excess of As(V) they contain, the lines of both As_2O_4 and As_2O_5 and no others (Patterns 5 and 6).

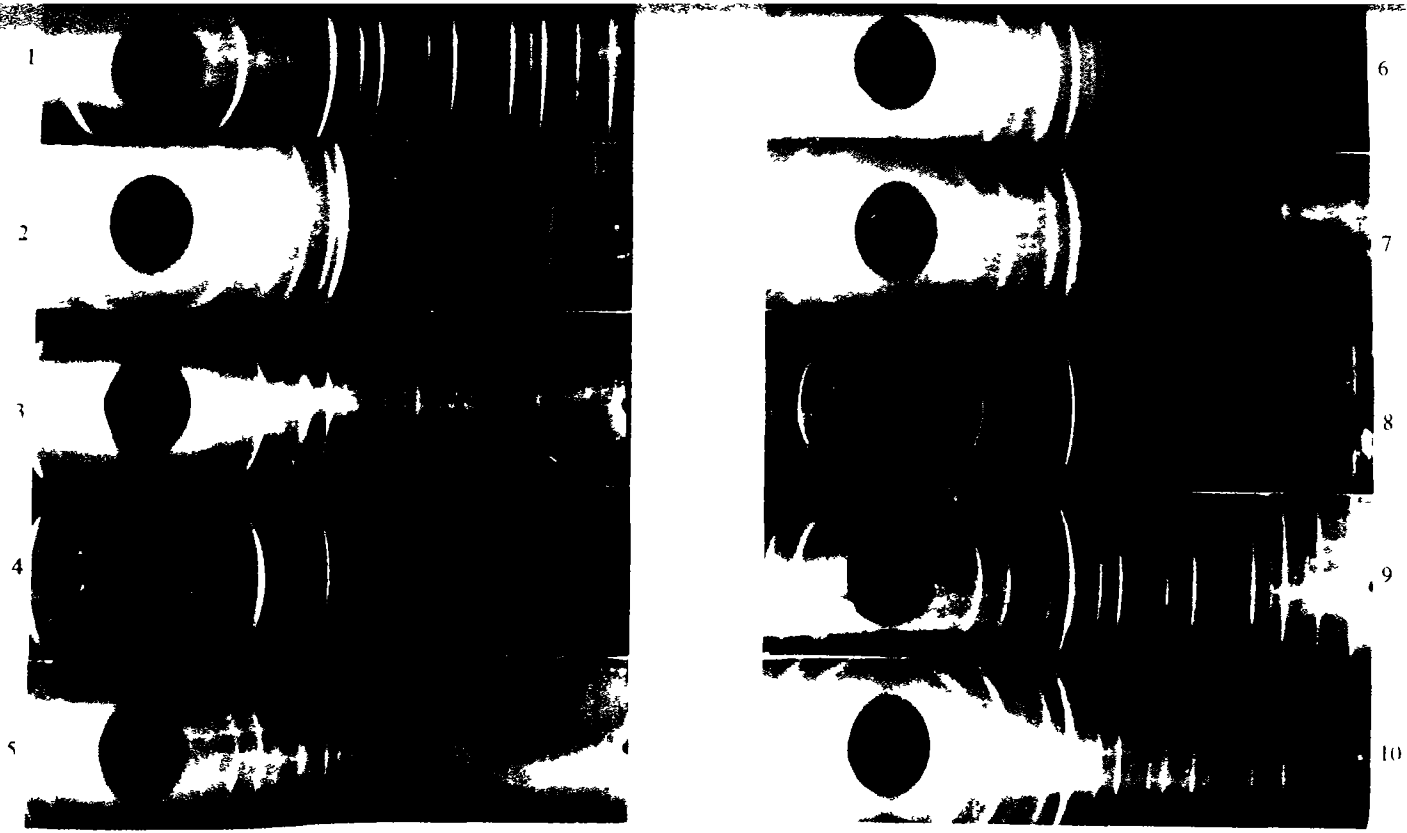


PLATE I. 1. As_2O_3. 2. As_2O_5. 3. As_2O_4 from an equimolecular mixture of As_2O_3 and As_2O_5 with water at 110°C followed by drying at 400°C (analysis 49.5% As as As(III), 50.5% as As(V)) [Part I, Experiment (2.3)]. 4. $6As_2O_4.5H_2O$ from an equimolecular mixture of As_2O_3 and As_2O_5 with water at 110°C (50.8% As as As(III), 49.2% as As(V)) [Part I, Experiment (2.3) intermediate stage]. 5. Product from heating a dry equimolecular mixture of As_2O_3 and As_2O_5 at 400°C for 33 hr (41.6% As as As(III) as 58.4% as As(V)) [Part I, Experiment (1.2)]. 6. Product from heating a dry equimolecular mixture of As_2O_3 and As_2O_5 in a sealed tube at 400°C for 112 hr and in an open tube for 80 hr (42.3% As as As(III), 57.7% as As(V)) [Part I, Experiment (1.3)]. 7. Glass from burning As under 30 atm O_2 (70.2% As as As(III), 29.8% as As(V)). 8. Sublimate from burning As under 20 atm O_2 (84.6% As as As(III), 15.4% as As(V)). 9. Sublimate from burning As under 25 atm O_2 (77.0% As as As(III), 23.0% as As(V)). 10. Sublimate from burning As under 30 atm O_2 (72.9% As as As(III), 27.1% as As(V)).

Inorg. Nucl. Chem., 1963, Vol. 25, pp. 93 to 98. Pergamon Press Ltd. Printed in Northern Ireland

STUDIES ON ARSENIC TETROXIDE—III

DETERMINATION OF THE HEAT OF FORMATION

L. H. Long and J. F. Sackman*

Department of Chemistry, University of Exeter, Exeter

(*Received* 24 *July* 1962)

Abstract—The heats of solution in aqueous NaOH of a number of different As_2O_4 preparations have been measured. Comparison with the values given by As_2O_3 and As_2O_5 have shown that the reaction

$$\tfrac{1}{2}As_2O_3\ (\text{octahedral}) + \tfrac{1}{2}As_2O_5\ (c) \rightarrow As_2O_4\ (c)$$

is nearly thermoneutral with a heat of reaction ($-\Delta H$) of 0.7 ± 0.22 kcal/mole, from which the heat of formation of As_2O_4 follows. Although As_2O_4 appears to be capable of taking up either As_2O_3 or As_2O_5 over a wide continuous range of concentrations in the solid phase, no mixed oxide studied was found to be thermodynamically more stable than pure As_2O_4, and the thermochemical evidence supports other evidence that As_2O_4 is a distinct species. The values for mixtures of oxides obtained by combustion of arsenic in dry oxygen under pressure invalidate an earlier attempt to measure the heat of formation of As_2O_4.

Prior to the present study, the only published value for the heat of formation of As_2O_4 was an old one due to Britzke *et al.*(1) who gave -12.24 kcal/mole for the heat of the reaction

$$\tfrac{1}{2}As_2O_3 + \tfrac{1}{2}As_2O_5 \rightarrow As_2O_4 \qquad (1)$$

Apart from the fact that this result is unlikely, in that if As_2O_4 were so markedly endothermic with respect to the other oxides it would be unstable towards disproportionation, the method adopted in obtaining this value involved several unsatisfactory features. In principle it consisted of measuring the difference in the heats of solution of two preparations of mixed oxides of arsenic, the first prepared by burning arsenic in oxygen under pressure in a bomb, the second by treating part of the first mixture with ozone. The amounts of tri- and penta-valent arsenic in the mixtures were determined by analysis, so that from a knowledge of the heats of solution of As_2O_3 and As_2O_5, the heat of solution of the As_2O_4 assumed to be present could be calculated and a figure for its heat of formation deduced. However the interpretation of the analytical data is not unique, since a number of assumptions were involved: firstly, that on burning arsenic under pressure all the pentoxide formed combines with the trioxide present in excess to give tetroxide, which has already been found in Part II(2) to be false; secondly, that on treating such a mixture of trioxide and tetroxide with ozone some of the trioxide is converted directly to pentoxide without the formation of tetroxide (in point of fact the treatment with ozone was discontinued after only a small amount of oxidation had taken place, leaving a mixture that was supposed to contain mainly the trioxide and tetroxide, with a little pentoxide); thirdly, that none of the tetroxide is oxidized by the ozone; and fourthly (tacitly), that no peroxy-compound is produced by the ozone. These assumptions are at least in part incorrect, and since, further, it had been found that arsenic trioxide produced in the bomb is originally largely present as an energy-rich modification[2] (which moreover changes its heat of solution on exposure to atmospheric moisture), of which fundamental fact BRITZKE *et al.* were obviously unaware, a redetermination of the heat of formation of As_2O_4 by a more satisfactory method was necessary. In undertaking this, the better-characterised specimens of As_2O_4 prepared according to the procedures described in Part I[3] were used.

---

* Present address: A.W.R.E., Aldermaston, Berks., U.K.

F. V. Britzke, A. F. Kapustinskii and L. G. Chentzova, *Z. Anorg. Chem.* **213**, 58 (1933).
L. H. Long and J. F. Sackman, *J. Inorg. Nucl. Chem.* **25**, 87 (1963).

The method was to measure the heat of solution of the As_2O_4 specimens in dilute caustic soda and compare the values obtained with that given by an equimolecular mixture of dry As_2O_3 and As_2O_5. The difference provided the heat of reaction (1) directly, the only assumption being that, on dissolution in sodium hydroxide, As_2O_4 yields a solution which in no way differs from that given by the As_2O_3–As_2O_5 mixture. As the resulting solutions exhibit the same reactions and are in all other observed respects similar, there is no reason to doubt the validity of this assumption. Further, since it was checked that the heat of solution of an unheated mixture of trioxide and pentoxide is experimentally indistinguishable from the total heat liberated when the trioxide and pentoxide are dissolved separately, no error arises through any heat of mixing of arsenious and arsenic acids in solution, and the correction for the presence of small amounts of free As_2O_3 or As_2O_5 in the tetroxide samples is a simple arithmetic one.

EXPERIMENTAL

Apparatus

The calorimeter consisted of a straight-sided Dewar flask of 600 ml capacity immersed to its rim in a constant temperature water-bath fitted with a thermometer and stirrer. The neck of the flask was closed with a large rubber bung through which passed a rotary glass stirrer, a Beckmann thermometer, a heating coil and an ampoule crusher. The whole apparatus was kept in an electrically heated enclosure thermostatically maintained at 25° C ± 0.25° C, a temperature slightly above the working temperature.

Since 1.872N sodium hydroxide solution was to be used as the calorimeter liquid in the solution experiments, the thermal constants of the calorimeter system were determined with a standard quantity (250 ml) of this liquid in the calorimeter. Because the speed of stirring needed to be varied according to requirements, the heat rises due to stirring and heat transfer were determined separately for each experiment by following the change in temperature for 10 min periods immediately before and after each run. A typical value for the stirring was 0.005° C/min, and although the variation between the runs was small, it was significant enough to warrant individual determination.

The heat capacity of the calorimeter system was determined by partially neutralizing 1.872N sodium hydroxide as the calorimeter liquid with known weights of standard 16N sulphuric acid. The acid was introduced in thin-walled glass ampoules; about 1.1 g gave the required temperature rise of 0.8° C. Mixing with the alkali was effected at the appropriate moment by crushing the ampoule with the ampoule crusher and the rise in temperature noted. From a knowledge of the heats of formation of water, H_2SO_4 (*aq*), NaOH (*aq*) and Na_2SO_4 (*aq*) at the appropriate dilutions[4] the heat liberated could be calculated, and hence the heat capacity from the corrected temperature rise. The mean of six determinations thus obtained was 272.61 g for the standard system, with a mean deviation of 0.19 per cent and a maximum deviation of 0.29 per cent.

Materials

As_2O_3 was A.R. material dried at 200° C.

As_2O_5 was prepared from As_2O_3 by heating it with excess A.R. concentrated nitric acid near the boiling point of the latter for several hours after solution was complete. The solution was then evaporated under reduced pressure until a solid was formed, which was freed from the last traces of nitric acid and moisture by heating it to constant weight at 350 C The resulting solid was shown by analysis to be pure As_2O_5 and was stored in a vacuum desiccator

---

[3] L. H. LONG and J. F. SACKMAN, *J. Inorg. Nucl. Chem.*, **25**, 79 (1963).

[4] F. D. ROSSINI, D. D. WAGMAN, W. H. EVANS, S. LEVINE and I. JAFFE, *Selected Values of Chemical Thermodynamic Properties*. National Bureau of Standards, Circular No. 500, Washington (1952).

As_2O_4 was prepared from As_2O_3 and As_2O_5 according to the various dry and wet procedures described in Part I [3] Different preparations were studied separately Some of these preparations were nearly pure, but others contained considerable quantities of free As_2O_5 as revealed by analysis and X-ray studies [4] However, as they had all been heated to constant weight at a temperature where free As_2O_3 would have sublimed, it could be assumed that all the trivalent arsenic present was combined in the form of As_2O_4, so that the preparations were treated as As_2O_4 admixed with As_2O_5

Procedure

Weighed quantities of each oxide were sealed off in thin-walled glass ampoules similar to those used in the determination of the heat capacity of the system Each ampoule was opened under 250 ml of 1 872N sodium hydroxide by means of the ampoule crusher, and the temperature rise noted for complete dissolution Appropriate corrections were applied to the observed temperature rise as in the calibration experiments The quantities of As_2O_3 As_2O_5 and As_2O_4 required to give a convenient rise in temperature were 3, 0 7 and ~1 g respectively Previous workers[7] had found that the dissolution of As_2O_3 was exceedingly slow, due to difficulties in wetting Accordingly, the behaviour of the oxide was observed in control experiments using an unsilvered Dewar flask These revealed that on crushing the ampoule under NaOH solution the As_2O_3 tended to trap bubbles of air which formed a cushion round the oxide, thus preventing proper contact with the solution However it was found that the tendency to trap air largely disappeared if the trioxide was kept in an oven at 110 C until immediately before use Accordingly, the filled ampoules were maintained at this temperature for some time before they were sealed off, and with this precaution complete dissolution was subsequently effected within 20 min The As_2O_5 and As_2O_4 samples were likewise sealed off at 110 C and in these cases dissolution was completed in 7-8 min

RESULTS

Heat of solution of As_2O_3 in aqueous NaOH

Of the eight experiments carried out with As_2O_3 as described above seven were in good agreement and accorded with a corrected mean of 61 5 0 5 cal g This figure refers to the dissolution of 3 07 g of As_2O_3 in 250 ml of 1 872-N NaOH, and corresponds to 12 16 0 10 kcal mole

Heat of solution of As_2O_5 in aqueous NaOH

All seven experiments carried out with As_2O_5 agreed well and yielded a corrected mean of 378 7 2 cal/g This figure refers to the dissolution of 0 736 g of As_2O_5 in 250 ml of 1 872-N NaOH and orresponds to 87 07 0 28 kcal/mole

eat of solution of As_2O_4 in aqueous NaOH

Eight different preparations of As_2O_4 produced by seven different procedures described in Part I [3] ere studied The products contained varying amounts of free As_2O_5 (but since they had been heated constant weight at 350-400 C no free As_2O_3) the As_2O_4 content ranging from 82 1 to 99 0 per cent weight The results are expressed in Table 1, the modes of preparation given in the second column ing designated as in Part I Comparison is made with the heats of solution calculated for equivalent xtures of uncombined As_2O_3 and As_2O_5, and the difference expressed in kilocalories per mole of $_2O_4$ It is seen that the value obtained is dependent on the purity and probably in the case of pure samples also on the mode of preparation

eats of solution in aqueous NaOH *of oxides prepared from the combustion arsenic in oxygen under pressure*

Samples of the oxide mixtures prepared by burning powdered elementary arsenic in a bomb filled h dry oxygen under pressure according to the procedure described[2] in Part II were sealed off in poules as before with the minimum exposure to atmospheric moisture The calorimetric results dissolving samples prepared at three different pressures of oxygen are recorded in Table 2 The ferences in the last column cannot be expressed in terms of moles of As_2O_4 since as discussed in rt II[2], the evidence is that these preparations contain both free As_2O_3 and free As_2O_5 Accordingly trivalent arsenic is here everywhere in excess, the difference is expressed per mole of As(V)

J THOMSEN, *Thermochemische Untersuchungen* Vol 2 Barth, Leipzig (1882)

7

TABLE 1.—HEATS OF SOLUTION OF ARSENIC TETROXIDE PREPARATIONS IN 1.872 N AQUEOUS SODIUM HYDROXIDE

Sample No.	Mode of preparation (see Part I)	Ratio As(III)/As(V)	Purity (% As_2O_4)	No. of runs	Heat of solution		Difference	
					Calc. for As_2O_3–As_2O_5 (cal/g)	Observed (cal/g)	per g oxide (cal)	per mole As_2O_4 (kcal)
1	1.1	0.753	85.0	5	253.86	260.38 ± 0.7	6.52	1.64
2	1.2	0.712	82.1	5	258.30	263.39 ± 0.9	5.09	1.33
3	1.2	0.721	82.8	5	257.19	262.06 ± 0.6	-4.87	-1.26
4	1.3	0.814	89.1	5	247.99	253.64 ± 1.1	5.65	-1.36
5	1.4	0.810	88.8	5	248.43	247.07 ± 0.6	-1.36	-0.33
6	2.1	0.945	97.0	5	236.41	233.29 ± 0.7	3.12	0.69
7	2.2	0.780	86.9	4	250.94	254.80 ± 0.4	3.86	0.95
8	2.3	0.982	99.0	5	233.43	230.23 ± 0.6	-3.20	-0.69

TABLE 2 - HEATS OF SOLUTION IN 1.872 N AQUEOUS SODIUM HYDROXIDE OF THE OXIDE MIXTURES OBTAINED FROM BURNING ELEMENTARY ARSENIC IN OXYGEN UNDER PRESSURE IN A BOMB

Initial O_2 pressure in bomb (atm)	Ratio As(III)/As(V) in oxide	Heat of solution: Calc for As_2O_3 As_2O_5 (cal/g)	Heat of solution: Observed (cal/g)	Difference: per g oxide (cal)	Difference: per g-atom As^V (kcal)
20	5.48	117.0	122.5 ± 0.5	5.5	3.6
25	3.89	134.5	143.9 ± 0.7	9.4	4.7
30	3.12	147.5	160.6 ± 0.8	−13.1	5.6

DISCUSSION

The markedly negative values in the last column of Table 2 correspond to a very pronounced endothermicity with respect to As_2O_3–As_2O_5 mixtures. The poor agreement in the last column suggests that this endothermicity is not to be associated with the pentavalent arsenic. That it is rather to be associated with the free As_2O_3 present is clear from the very anomalous rapidity with which the As(III) goes into solution in contact with water, as described in Part II.[2] The endothermicity is probably even greater than that indicated in Table 2, since it falls very rapidly in contact with moisture, and the total exclusion of atmospheric moisture during the operation of filling the ampoules was in practice not feasible. Clearly the experiments recorded in Table 2 provide no information regarding the heat of formation of As_2O_4 other than to suggest n explanation for the anomalous, highly endothermic value for the heat of reaction 1) reported[1] by BRITZKE and co-workers, who utilized oxides similarly prepared in a bomb. It is now seen that no reliance whatever can be placed on their method.

To derive the heat of formation of As_2O_4 it is necessary to resort to the results ported in Table 1. Broadly speaking, these results indicate that the purer the As_2O_4 e more exothermic it becomes. This is not surprising if lattice distortions caused by e presence of As_2O_5 as impurity enhance the energy of the As_2O_4 lattice. The first 5 mples were all prepared by the dry method, and, of these samples 1–4 inclusive gave ther similar results. Although of a similar purity to sample 4, sample 5 proved to be ch more exothermic. This was the only sample to have been reheated with a second antity of As_2O_3. As very little further As_2O_3 was taken up, the explanation probably ts in the effect of contact with atmospheric moisture during and after the regrinding h further As_2O_3 (the suggestion being that moisture is necessary to enable the newly med As_2O_4 to release the strain in its lattice). At all events, except for the highly pure sample, for which the essential preheating was omitted (Part I, Experiment 2)), the products from the wet method are the most exothermic. Moreover, samples nd 8 with the highest exothermicity are by far the purest, and with purity 97.0 and 0 per cent respectively these are the only two which need to be considered in the l result. Each value rests on five separate runs, and the very close agreement implies t a sample of 100 per cent purity would yield a value not significantly different ction (1) is thus seen to be close to thermoneutral. With the final experimental re of 0.7 kcal/mole for the heat of reaction (−ΔH) must be associated a random r of 0.22 kcal/mole.

The heat of formation of As_2O_4 can now be calculated from the corresponding values for the trioxide and pentoxide The ΔH_f values given[4] in the latest compilation are 156 97 and 218 6 kcal/mole for As_2O_3 (octahedral) and As_2O_5 (c) respectively These values however correspond to ΔH 74 9 kcal/mole for the reaction

$$As_2O_3(aq) + O_2(g) \rightarrow As_2O_5(aq) \tag{2}$$

whereas BJELLERUP *et al* by a more direct method have recently found[6] 78 0 kcal/mole for reaction (2) and this is doubtless the more reliable figure Since in the compilation[1] the heats of formation of the crystalline oxides are derived from the values for the aqueous forms in combination with the respective heats of solution, it follows that the difference between the values for As_2O_3 (octahedral) and As_2O_5 (c) needs to be increased by 3 1 kcal/mole That for As_2O_3 (octahedral) is the better-established value, being based on the free energy of formation calculated from cell measurements[7] together with entropy data,[8] and is closely supported (to within about 0 2 kcal/mole) by the more recent data [9]of KIRSHNING and PLIETH, whereas the value for As_2O_5 (c) rests solely on early work[5] by THOMSEN Accordingly following a recommendation[10] from the National Bureau of Standards, we here adopt the amended value - ΔH_f 221 7 kcal/mole for As_2O_5 (c) Combination of the foregoing values for the heats of formation with the experimentally derived figure of 0 7 kcal/mole for the heat of reaction (1) gives 190 0 kcal/mole for the heat of formation of As_2O_4 (c)

[6] L BJELLERUP S SUNNER and I WADSÖ *Acta Chem Scand* **11**, 1761 (1957)

[7] R SCHUHMANN, *J Amer Chem Soc* **46**, 1444 (1924)

[8] K K KELLEY *Contributions to the Data on Theoretical Metallurgy, XI Entropies of Inorganic Substances* U S Bur Mines Bulletin No 477 Washington (1950)

[9] H J KIRSHNING and K PLIETH *Z Anorg Chem* **280**, 346 (1955)

[10] W H EVANS Private communication (1961)

J Inorg Nucl Chem 1963 Vol 25 pp 99 to 102 Pergamon Press Ltd Printed in Northern Ireland

SOLUBILITIES AND EFFECTIVE OXIDATION STATES OF SOME LOWER MOLYBDENUM CHLORIDES IN CONCENTRATED SULPHURIC ACID AND RELATED SOLVENTS

L J BAILIN* and H B JONASSEN
Department of Chemistry, Tulane University New Orleans

(*Received* 1 *February* 1962, *in revised form* 11 *June* 1962)

Abstract The solubilities and effective oxidation states of molybdenum ions resulting from the dissolution of $MoCl_3$ and K_3MoCl_6 in concentrated H_2SO_4 were determined At room temperatures the oxidation state was 3 0 at 180 C, from 4 5 to 4 8 $MoCl_3$ in contact with SO_3 reacted via surface reaction only, K_3MoCl_6 formed reversible adducts with SO_3 from 64 to 180 Both $MoCl_3$ and K_3MoCl_6 reacted with fuming sulphuric acids to yield highly coloured solutions Based on similarities in colour vs SO_3 content in the fuming acids and reversible K_3MoCl_6—SO_3 adduct formation, it is postulated that the effective oxidation states are also 3 0 4 8 within the specified temperature limits for these solutions

IN the course of investigating electrolyses of concentrated sulphuric acid systems containing lower valence molybdenum chlorides[1] a number of solutions were prepared which were either unknown or sparsely described in the literature Molybdenum(III) chloride was reported to dissolve in concentrated H_2SO_4 to form a blue coloured solution, which on heating turned emerald green [2] A second reference reported the general solubility of $MoCl_3$ in H_2SO_4,[3] but in neither source were oxidation r measured solubilities discussed No information on K_3MoCl_6 in H_2SO_4 was found Because of this lack, a study of the solubilities and oxidation states of the molybdenum ons in solution was undertaken

Molybdenum(III) chloride and potassium hexachloromolybdate(III) chloride were acted with C P concentrated sulphuric acid, two fuming sulfuric acids and gaseous O_3 Sulphur trioxide was included on the basis of preliminary work which indicated at colour formation might correlate with per cent available SO_3 in the solvents

EXPERIMENTAL

agents

Anhydrous molybdenum(III) chloride was obtained from A D Mackay Inc, New York tassium hexchloromolybdate(III) from the S W Shattuck Chemical Company Denver Colorado All concentrated and fuming sulphuric acids were Baker Analysed Reagent grade

eparation of solutions

1 $MoCl_3$ *in hot* 96% H_2SO_4 To 8 07 g $MoCl_3$ in a 125 ml Erlenmeyer flask were added 187 0 g 4% H_2SO_4 to give a 4 14 per cent mixture, which was heated for 2 hr under dry nitrogen at 180 e resulting solution was olive green after the first hour During the reaction HCl was evolved wly Some $MoCl_3$ remained at the end of the heating period Further heating at 300 310, the

---

* Now at Research and Engineering Laboratories, Lockheed Missiles and Space Company Palo o, California

L J BAILIN Dissertation, Tulane University (1958) L C Card No Mic 59 61

W MELLOR, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry* Vol II p 620 ongmans, Green, New York (1930)

M COMEY, *A Dictionary of Chemical Solubilities*, MacMillan New York 231 (1876)

ature of the system resulted in complete solution and colour fade to a light yellow
in cold 96% H_2SO_4 To 2 0 g $MoCl_3$ were added 55 1 g 96 4% H_2SO_4 Mixing was
t ambient temperatures for 24 hr in a stoppered flask Centrifuging the 3 5 per cent
led a weakly coloured blue solution The solid residue contained most of the original

in fuming H_2SO_4 15 18 *and* 30 33% SO_3 A 4 8 per cent solution of $MoCl_3$ in 15–18
fuming H_2SO_4 was prepared by refluxing for 2 hr at 170-180 The solution was dark
urther refluxing at 180 for 4 hr showed no further colour change No residue remained
cent solution of $MoCl_3$ in 30 33 per cent SO_3 fuming H_2SO_4 was prepared in a similar
fluxing at 120 125 The final colour of the solution was bright blue, and the time
omplete dissolution was less than 1 hr
l_6 *in hot* 96% H_2SO_4 A 4 94 per cent solution of K_3MoCl6 in 96 per cent H_2SO_4 was
ow dropwise addition of the acid to the solid in a 50 ml round bottom flask fitted with a
umes of HCl were released rapidly during the addition After the major part of the
ed, the mixture was heated to accelerate solution At 190 , the solution was dark green,
no solids remaining
l_3 *in cold* 96% H_2SO_4 A 3 9 per cent mixture was prepared in the cold as above
n of the suspension yielded a red-brown solution
l_3 *in fuming* H_2SO_4 15 18 *and* 30 33% SO_3 Two 7 0 per cent solutions were prepared
vise addition of the respective fuming acids onto K_3MoCl_6 HCl was given off volumi-
ing to the reflux temperatures, 170 180 and 120–125 yielded dark blue solutions
he colour development in the 30 33 per cent acid, however occurred more rapidly than
, SO_3 acid No residue remained

sulphur trioxide adducts

A complete description is found in Reference 1 The following summarizes the
res
$_2SO_4$ 30 33% SO_3, was used as source for SO_3 About 50 ml of the acid were placed
und flask which contained a well for thermometer placement Commercially available
which was used as carrier gas, was passed through a hot tube filled with copper turnings
es of oxygen, and then bubbled through the heated acid via a capillary bleed tube, the
vas positioned about ½ in below the surface of the acid Temperatures for efficient
ranged from 115 to 125 The SO_3-N_2 mixture was passed through a fine porosity
ter tube to remove brownish-black decomposition products formed during the heating
acid The filter was placed well within the reaction tube to prevent liquefaction of the
atures were measured by placing a thermometer at a fixed position over the reaction
rating against materials of known melting point placed in the boat
Two to five grammes of sample were weighed into a Vitreosil silica boat and inserted
on chamber maintained at a pre-chosen temperature in an electric tube furnace Pre-
K_3MoCl_6 was necessary to remove small amounts of moisture the solid was heated in
be under nitrogen at 110 120 for 2 hr The dry nitrogen under a slight excess pressure
n the heated fuming acid and carried the evolved SO_3 through the filter tube into the
per
SO_3 Reaction began at 80 with the formation of a grayish black coating With the
creased coverage of the surface, no other changes were observed as the temperature was
al examination of the final product indicated surface reaction only Changing the
$MoCl_3$ particle size SO_3 evolution rate, etc did not effect further reaction Decom-
ed without melting under the SO_3–N_2 atmosphere at 200-220 yielding varied coloured
a control run, $MoCl_3$ under dry nitrogen was stable up to 260°
l_6 SO_3 In a similar control run under dry nitrogen, K_3MoCl_6 was stable up to 250°
the $MoCl_3$–SO_3 system when SO_3 was passed over the K_3MoCl_6, reaction occurred
and continued up to 190° before decomposition became obvious at 200–210° Equilib-
from 64° to 180° yielded a liquid phase having colours ranging from dark blue at the
-80 , to bluish green at the intermediate range, 80 –165°, and dark green at the high
0

m was determined gravimetrically using 8-quinolonol Chloride was determined
with standard mercuric nitrate using sodium nitroprusside as indicator
on state of molybdenum was determined as follows excess standard potassium di-
entrated sulphuric acid solution was used to oxidize the molybdenum in solution and
ucts to the maximum valence of six The unreacted dichromate was found by titration

standard aqueous ferrous sulphate (1) The figures obtained are effective oxidation numbers, and fore are only average values

he sulphur trioxide values were calculated on the basis that increase in weight of the adduct is utable to the addition of SO$_3$ to K$_3$MoCl$_6$ See discussion for justification of this assumption

RESULTS AND DISCUSSION

able 1 summarizes the solubility data and oxidation numbers for MoCl$_3$ and oCl$_6$ in concentrated H$_2$SO$_4$ The valence states show oxidation to about the levels for the heated solutions, and are probably mixtures of molybdenum 3

TABLE 1 —SOLUBILITY AND EFFECTIVE OXIDATION NUMBER FOR MOLYBDENUM ION IN CONCENTRATED SULPHURIC ACID

System	Temperature	% Mo in solution	Calculated % solubility of salt	Colour	Effective oxidation no
oCl$_3$-H$_2$SO$_4$	Ambient	0 0828	5 1	Light blue	3 02
oCl$_3$-H$_2$SO$_4$	180	1 99	100	Olive green	4 8
$_3$MoCl$_6$-H$_2$SO$_4$	Ambient	0 768	87	Red brown	2 98
$_3$MoCl$_6$ H$_2$SO$_4$	180°	1 11	~ 100	Dark green	4 5

igh 6 The 180° systems show essentially complete dissolution Table 2 summa- the adducts of SO$_3$ with K$_3$MoCl$_6$ formed reversibly at several temperatures ence for reversibility in the 64° to 180° range was shown by constancy of the six to Cl/Mo ratio, the molybdenum oxidation state, and the ease by which SO$_3$ could be

TABLE 2 — SULPHUR TRIOXIDE ADDUCTS OF K$_3$MoCl$_6$ AT VARIOUS TEMPERATURES

Temperature	No equivalent SO$_3$ molecules	Colour	Effective oxidation no
64	10	Dark blue	3 0
137	8	Dark blue–green	3 0
155	6	Green-dark blue	3 0
165	5	Green blue	3 0
180	4	Green	3 0
194		Dark brownish green	4 0

l to or removed from a given sample by adjustment of the reaction temperatures (1) the presence of the SO$_3$ atmosphere, the weight of an adduct invariingly in- ed as the temperature was lowered, the weight decreased in a similar way as the erture was raised For a given temperature, the per cent increase over the original oCl$_6$ weight was constant irrespective of the direction from which this tempera- was attained As a check of the constancy of the six to one Cl/Mo ratio in the t the reaction chamber effluent was analysed for Cl, none was found, thus ing that addition reactions indeed had occurred

e 4 0 oxidation number for the adduct formed at 194° is consistent with the colour e and gas evolution which occurred within the decomposing liquid at that tem- ure, and is included as an approximate upper limit of reversibility The Cl/Mo for this adduct was 5 1 indicating loss of Cl during the decomposition t determinations of the oxidation states in the fuming acids were impractical, and t would have yielded questionable values Therefore, by analogy with the colours is obtained in 2 M HNO_3 about half of the RuO_4 would be protonated which should be easy to detect.

In the present work MARTIN's assumption has been further examined by electromigration and spectrophotometric measurements.

EXPERIMENTAL

Materials. Most measurements were made using ^{103}Ru ($T_{1/2}$ = 40 days, γ-ray energy 0.5 MeV) supplied by the Radiochemical Centre, Amersham, England. Solutions of RuO_4 in nitric acid were prepared from A.R. $RuCl_3$ by dissolution in 6 N H_2SO_4, boiling till evolution of white fumes and oxidizing with sodium bismuthate.(11) The RuO_4 was distilled at 100° and collected in the appropriate nitric acid solution. The yield of this preparation process was usually 99 per cent. The concentration of the RuO_4 in most experiments varied between 10^{-5} and 10^{-3} M, except for the solubility experiments. Ru(III) solutions in nitric acid were prepared by adding silver nitrate to the $RuCl_3$ solution in nitric acid and filtering.

Electromigration experiments. The apparatus is described in Fig. 1. It consists of a horizontal central compartment *B* with an inlet funnel in its centre and two sintered glass diaphragms *D* at both ends. The anode and cathode compartments *A* and *C* are connected by salt bridges *L* to the electrode vessels *I*. The central part is water cooled to avoid loss of RuO_4 by evaporation. The apparatus was filled with acid of the same concentration throughout. A d.c. voltage of 110 V was applied and currents were between 40 and 60 mA. After a few hours samples were taken from all three compartments.

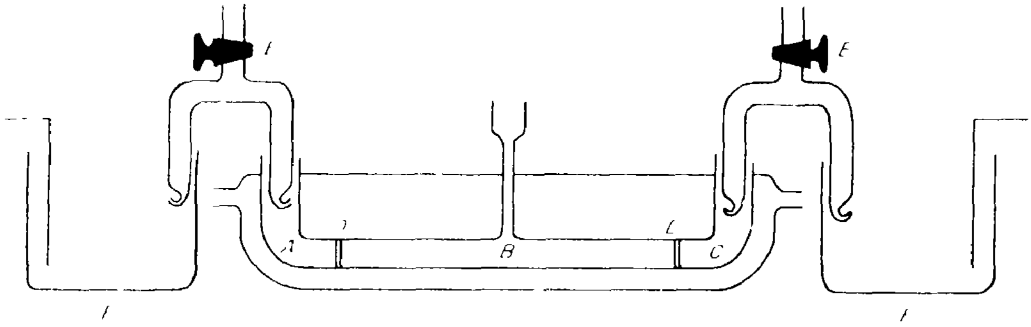


FIG. 1. Electromigration apparatus.

Spectrophotometric measurements. Spectra were measured with a Beckman DU or Unicam SP 500 Spectrophotometer, using 10 mm cells. In some experiments sodium hypochlorite was added to avoid reduction of the RuO_4. A small error is always introduced by decomposition of RuO_4 on the ground surface of the cell stopper. In later experiments a Cary Model 14 recording spectrophotometer was used.

Measurements of distribution coefficients. These were carried out by vigorous mixing of the two phases in a centrifuge tube. Care was taken to avoid reduction of the tetroxide during extraction by avoiding reducing organic impurities.

Solubility experiments. Labelled RuO_4 was distilled by the method described above into nitric acid solution cooled in an ice-bath and samples were taken until no increase in activity was observed. The temperature of the solution varied between 2–5°C but the error introduced by this is of the order of the experimental accuracy only.(12) The concentration was in this case also determined by adding 1 ml of the nitric acid solution to 50 ml 8 N NaOH. The ruthenium is thereby transformed to perruthenate and can be determined spectrophotometrically at 385 m*μ*.

Extraction of ruthenium into organic solvents by oxidizing it to RuO_4. A concentrated sodium hypochlorite solution was added to the Ru(III) solution and the extraction was performed as described above. The hypochlorite solution was prepared by passing chlorine through 11 M NaOH.

RESULTS AND DISCUSSION

The electromigration experiments showed no well defined migration in either direction (Table 1).

---

(11) R. P. LARSEN, L. E. ROSS and G. KESSER, U.S.A.E.C. Report ANL-5810 (1957).

(12) H. REMY, *Angew. Chem.* **39**, 106 (1926).

TABLE 1. ELECTROMIGRATION OF RuO_4 IN NITRIC ACID SOLUTION
(Initial specific activity of solution in central compartment between 1500 and 2000 counts per min per ml)

HNO_3 (M)	Current (mA)	Time (hr)	Specific activity (count min^{-1} ml^{-1}) Cathode	Anode
			Ru (VIII)	
11.0	55	4	54	52
2.7	30	24	67	84
1.0	60	3	40	62
1.0	60	18	145	190
2.7	0	12	137	80
			Ru (III)	
1.0	50	3	377	0
			$KMnO_4$	
1.0	40	1.2	No colouration	Pink colouration

From the control experiments with no current and with Ru(III) solution instead of RuO_4 it is clear that the activity in the anode and cathode compartment comes from diffusion only.

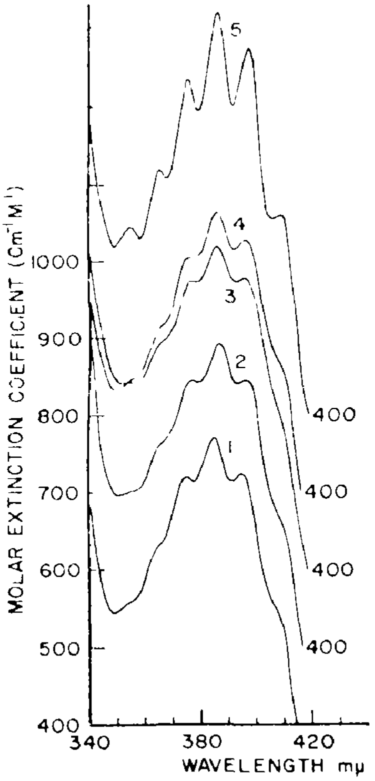


FIG. 2. Absorption spectra of RuO_4 solutions (1) in water (2) in 3 M HNO_3 (3) in 7.5 M HNO_3, (4) in 12 M HNO_3 (5) in CCl_4. The curves have been displaced vertically by 100 ordinate units for sake of clarity.

Qualitative experiment with permanganate ions showed a well defined migration of the coloured anions It may therefore be concluded that no charged species is formed when RuO$_4$ is dissolved in nitric acid

Fig 2 shows the spectra of RuO$_4$ in CCl$_4$, water and three nitric acid solutions of different concentrations No differences except a sharpening of the peaks in CCl$_4$ can be detected The solutions do not absorb in any other region, up to 1200 mμ It can therefore be deducted that the RuO$_4$ molecule is identical in a non-polar solvent such

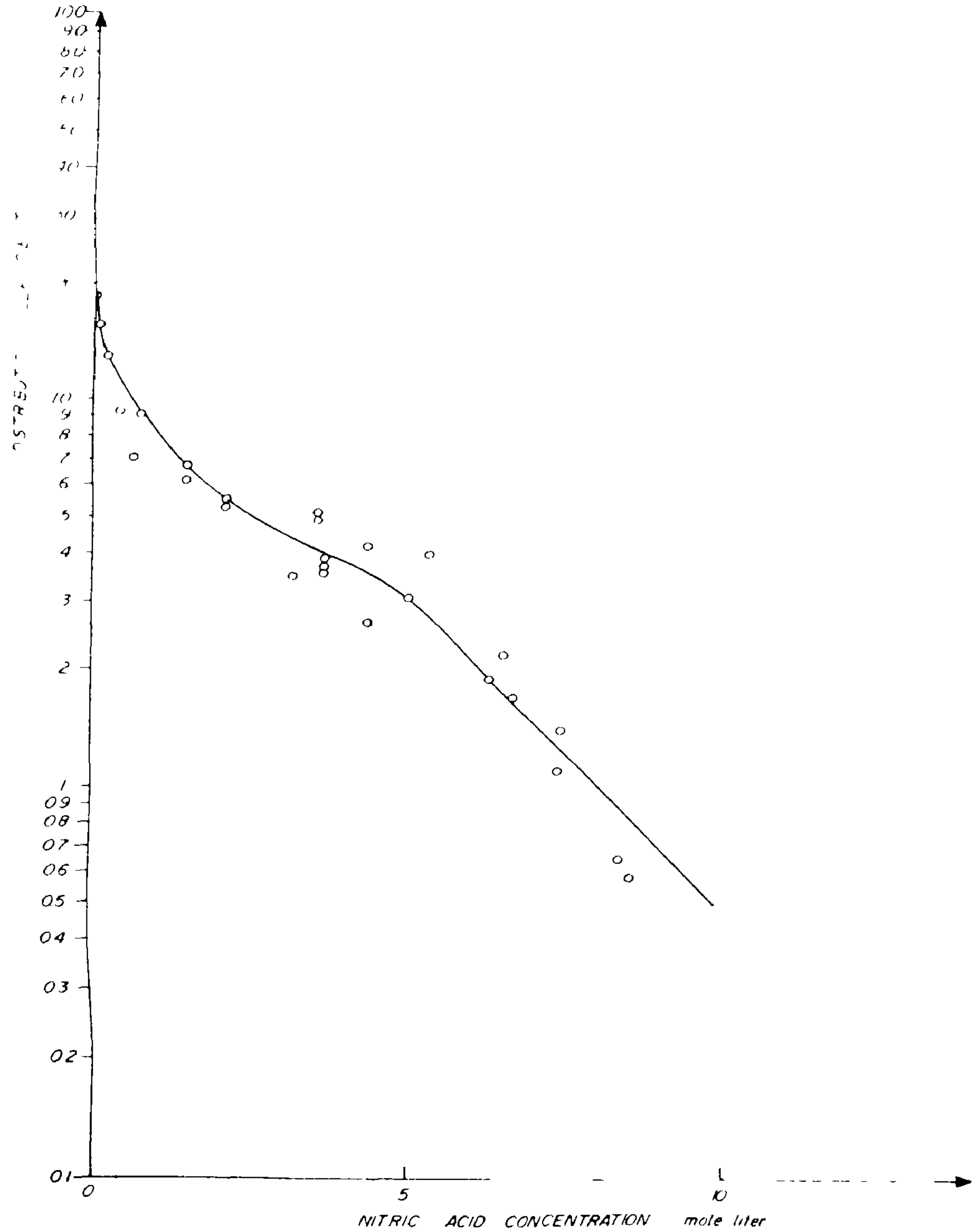


FIG 3 —Distribution coefficient of RuO$_4$ between nitric acid and kerosene

as CCl_4 and in 12 M nitric acid. Although earlier measurements of BRAUNE and STIEFE[6] gave two pairs of Ru-O distances, 1.66 and 2.74 Å respectively, DODD[7] later deduced from the infrared spectrum of RuO_4 that like OsO_4 it is a regular tetrahedron with Ru O distances of 2.23 Å. This work, like our results, does not support the reactions assumed by MARTIN[3].

Fig. 3 shows the results of the oxidative extraction of ruthenium by kerosene. Experiments were performed over a wide range of initial NaOCl concentrations. The deviations are rather large and therefore no quantitative expression for the kinetics could be derived. Although the distribution coefficients are rather low, and the salting effect of nitric acid is pronounced, this method would separate ruthenium specifically from fission product mixtures.

The results of the extraction experiments into CCl_4 are given in Fig. 4. The distribution coefficient decreases with increasing nitric acid concentration and increases with increasing sodium nitrate concentration. An attempt has been made to explain this behaviour by other means than formation of an ionic species.

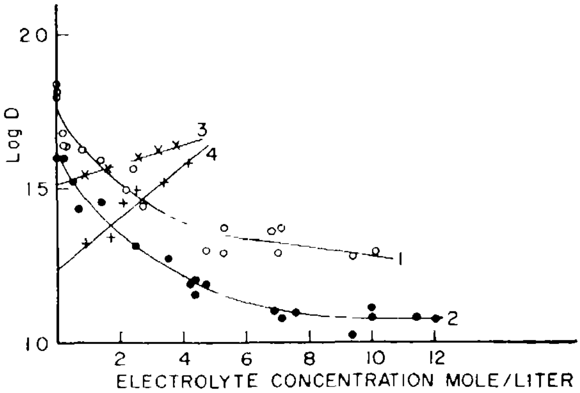


FIG. 4. Distribution coefficient of RuO_4 between nitric acid and or sodium nitrate and CCl_4.
(1) HNO_3, 20°C
(2) HNO_3, 0°C
(3) $NaNO_3$, 0.06 M HNO_3
(4) $NaNO_3$, 0.24 M HNO_3

It is of course possible to look at the RuO_4 simply as at a non-electrolyte dissolved in an electrolyte. The dependence of the distribution coefficient on the concentration of electrolyte can be explained as a salting effect: salting-in in the case of nitric acid and salting out in the case of sodium nitrate. The experimental salting coefficients according to the Setchenov equations are 0.13 liter mole^{-1} in the case of nitric acid and +0.04 l mole^{-1} in the case of sodium nitrate, compared to MARTIN's[3] values of 0.14 and +0.05 respectively.

Calculations of the salting coefficient according to McDEVIT and LONG[8] show positive salting coefficients up to 20°C, and a slightly negative coefficient at 25°C. Thus the salting behaviour should depend on the temperature. At low temperatures

---

[6] H. BRAUNE and K. W. STIEFE, *Angew. Chem.* **51**, 528 (1938).
[7] R. L. DODD, *Trans. Faraday Soc.* **55**, 1480 (1959).
[8] W. F. McDEVIT and F. A. LONG, *J. Amer. Chem. Soc.* **74**, 1773 (1952).

$NiYH_2O^{-2}$ (β) to NiY^{-2} (α, γ) similar to the case observed by SCHWARZENBACH(9) for CoY This argument is in agreement with the present results, since $NiYH_2O^{2-}$ will have a spectrum similar to that of $NiYHH_2O^-$, as in the case of $CrYH_2O$ and $CrYHH_2O$ (11) Also, it is not then necessary to assume that in the case of CuY^{2-} and CoY^{2-}, where geometrical isomers have not been reported, one water molecule is present in the first coordination sphere

In the case of normal copper and cobalt–EDTA complexes, it is difficult to understand why protonation of an already free carboxyl group should bring about the observed large differences in spectral intensities if we assume coordination by water On the other hand, breaking of one of the metal EDTA bonds with the introduction of new ligands like H_2O, NH_3 and OH^- can be expected to affect the absorption spectra appreciably with a trend similar to that observed here The present results, therefore, do not seem to lend much support to the assumption that one H_2O is attached to the metal atom in the normal complex, except possibly in the case of the β-nickel-EDTA complex of JORGENSEN

Comparison of stability constants

The formation constants of mixed complexes (obtained from MY^{2-}) of the type MYX may be expected to depend upon the $1/n \log \beta_n$ value of the MX_n complex The observed results show large deviations from this expectation, especially in the case of hydroxo-complexes of cobalt and nickel, e g , though OH^- is a stronger ligand than NH_3 the stability of the mixed ammino complexes were found to be greater This suggests that, besides the average strength of the metal-ligand bond, other factors, such as stereochemical, ligand field stabilization, etc , strongly influence the formation of mixed EDTA complexes KIDA(12) pointed out, from a study of series of complexes, that the formation of mixed complex is favoured when the ligands involved tend to stabilize the same geometrical configuration Since the ammino and EDTA complexes of Co(II) and Ni(II) are nearly octahedral, mixed complexes may be formed easily The hydroxyl ion does not appear to favour the octahedral structure In the case of copper the observed value for the hydroxo-complex is relatively high This may be attributed, as stated by JORGENSEN(10), to possible stabilization of the ground state due to intermixing of the electron transfer states

Acknowledgements—The authors wish to express their appreciations to Dr J SHANKAR, Head of Chemistry Division, Atomic Energy Establishment, Trombay, for his keen interest and useful suggestions and to Dr G S RAO for encouragement, during the course of the work

(11) C K JORGENSEN, *Acta Chem Scand* **9**, 1362 (1955)
(12) S KIDA, *Bull Chem Soc , Japan* **34**, 962 (1961)

J Inorg Nucl Chem 1963 Vol 25, pp 1155 to 1159 Pergamon Press Ltd Printed in Northern Ireland

NATURE, STABILITY AND BONDING OF THE PEROXY GROUP IN PEROXY TITANIUM COMPOUNDS

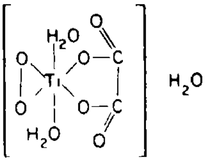
C C PATIL and G V JERE
Department of Inorganic and Physical Chemistry, Indian Institute of Science,
Bangalore 12, India

(*Received* 15 *December* 1962, *in revised form* 4 *March* 1963)

Abstract Some physicochemical properties of peroxy titanium compounds are explained by assigning a strained triangular ring structure to the peroxy titanyl group, with a bent and reduced overlap of the O O bonding orbitals The stability of the peroxy group is found to depend on the stability of the other ligands The decreasing order of stability of the peroxy group in the compounds is as oxalato maleato malonato sulphato peroxide of titanium

ORANGE red peroxy titanium complexes of oxalic,[1] malonic,[2] maleic[3] and sulphuric[4,5] acids were prepared in the solid state, but the corresponding complexes of organic monobasic acids (e g propionic acid) and fumaric and succinic acids could not be prepared because these complexes readily hydrolysed in solution Further, although peroxy titanium perchlorate was prepared in solution, it could not be obtained in the solid state, since, on evaporation even at room temperature, colourless crystals of titanyl perchlorate, $TiO(ClO_4)_2 6H_2O$, were obtained [6] The existence of peroxy titanium complexes of oxalic, malonic, maleic and sulphuric acids in solution and the solid state indicates that these acids function as bidentates, occupying two co-ordination positions When peroxy titanium compounds were kept in vacuum, the sulphate complex gave both ozone and oxygen while others gave only oxygen

It is unusual that even in presence of a large excess of hydrogen peroxide or the corresponding acid, the compounds retained one peroxy group and one dicarboxylate ligand Peroxy titanium sulphate, however, lost its orange red colour, when stored over strong sulphuric acid, probably due to the replacement of the peroxy group by a sulphate group The peroxy titanyl complexes may have structures of the type



Peroxy titanyl oxalate

---

[1] D P KHARKAR and C C PATIL, *Proc Indian Acad Sci* **44 A**, 287 (1956)
[2] G V JERE and C C PATIL, *Proc Indian Acad Sci* **57A**, 69 (1963)
[3] G V JERE and C C PATIL, Proc Symposium on Chemistry of Co-ordination Compounds Agra, Pt II, p 117, Natl Acad Sci, Allahabad, India (1960)
[4] M S MOHAN and C C PATIL, Proc Symposium on Chemistry of Co-ordination Compounds, Pt II, p 105, Natl Acad Sci Allahabad, India (1960)
[5] G V JERE and C C PATIL, *Canad J Chem* **40**, 1576 (1962)
[6] C C PATIL and V KRISHNAN, *J Sci Industr Res* (India), **20 B**, 604 (1961)

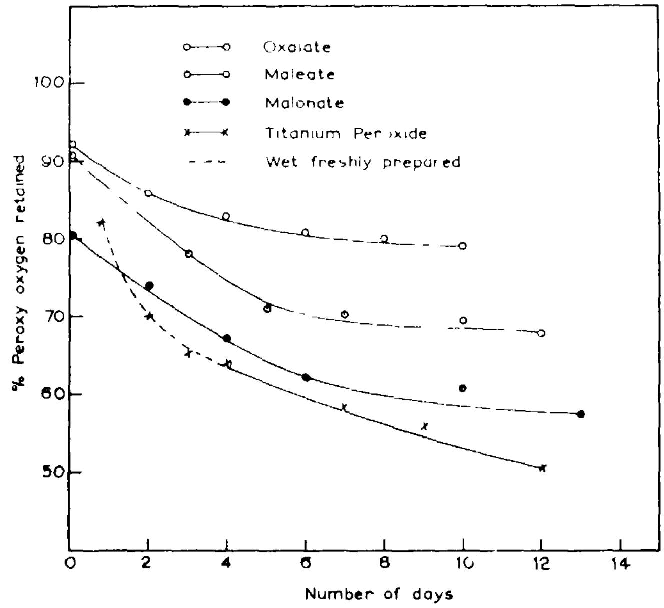


FIG 1 – Effect of storage on the peroxy oxygen content of peroxy titanium compounds

EXPERIMENTAL

The peroxy titanyl complexes employed had the ratio of Ti ligand H_2O 1 1 3, but the ratio of Ti O peroxy was not 1 1 even in the freshly prepared complexes in the solid state and it varied from 1 0 95 to 1 0 88 Light yellow hydrated titanyl peroxide had the ratio 1 0 65 These compounds, on storing in moisture-free atmosphere at room temperature (22–25 C), showed a slow and a continuous loss of peroxy oxygen, as shown in Fig 1 The rate of loss of peroxy oxygen is in the following order oxalato maleato malonato sulphato peroxide, the reverse of the peroxy oxygen contents of the freshly prepared compounds

Infra-red and electronic spectra

The infra-red spectra of peroxy titanium compounds were taken with Perkin-Elmer single beam spectrometer, model 112, employing nujol-mull technique and sodium chloride optic The observed bands for the peroxy group and the antisymmetrical and symmetrical vibration frequencies for O—C—O in the regions 1750 and 1400 cm^{-1} are given in Table 1

TABLE 1 —INFRA-RED BANDS OF PEROXY TITANYL AND O—C—O GROUP OF PEROXY TITANYL COMPOUNDS

Peroxy titanium compounds	TiO bands of $\mathrm{Ti}\begin{smallmatrix}\diagup\mathrm{O}\\ \vert\\ \mathrm{O}\end{smallmatrix}$ in cm^{-1}		O—C—O group bands (cm^{-1})	
	ν_1	ν_2	Antisymmetrical	Symmetrical
Oxalato	1062	870	1715	1390
Maleato	1080	890	1709	1429
Malonato	1041	891	1667	1443
Sulphato(5)	1005	870		
Peroxide(7)	1053	885		

---

(7) G V JERE and C C PATIL, *Z Anorg Chem* **319**, 175 (1962)

salting out should occur and only at 25°C salting in. This is not in accordance with the present experiments, which show salting in both at 0°C and at 25°C.

Similar calculations for sodium nitrate give a salting coefficient of 0.17 l mole^{-1}, compared with the experimental result of 0.04 l mole^{-1}. Attempts to explain these discrepancies have not been successful.

From the solubility data (Table 2) it is possible to calculate an interaction coefficient between the RuO$_4$ molecules themselves according to the equation[9]

$$\log \frac{f_i^0}{f_i} = k_s C_s - k_i(S_i - S_i^0) \qquad (6)$$

where f_i^0/f_i is the ratio of activity coefficients of saturated solutions in an electrolyte of concentration C_s and water respectively and k_s the salting coefficient at low concentration of the non-electrolyte which equals $(\log D/D_0)/C_s$. S_i^0 and S_i are the solubilities of RuO$_4$ in water and the electrolyte solutions expressed in mole/l. The interaction coefficient is shown in Table 3.

TABLE 2. SOLUBILITY OF RuO$_4$ IN NITRIC ACID AND ACTIVITY COEFFICIENTS OF THE SATURATED SOLUTIONS

HNO$_3$ concentration mole/l	Solubility mole/l	Activity coefficient
0	0.100	0.961
0.40	0.095	0.92
0.58	0.095	0.92
0.87	0.091	0.87
1.07	0.090	0.87
1.55	0.085	0.82
2.04	0.080	0.77
2.65	0.076	0.73
3.01	0.072	0.69
3.80	0.072	0.70
4.00	0.071	0.69
4.87	0.072	0.69
5.06	0.067	0.64
5.16	0.073	0.70

TABLE 3. INTERACTION COEFFICIENT BETWEEN RuO$_4$ MOLECULES FROM EQUATION (6)

HNO$_3$ conc. (mole l^{-1})	Solubility (mole l^{-1})	Log D/D_0 (Fig. 4)	k_i
0	0.100		
0.4	0.105	0.048	5.4
0.87	0.110	0.104	6.2
1.55	0.118	0.175	5.7
2.04	0.125	0.227	5.2

The mean value of k_i is 5.6 l mole^{-1}.

It is also possible to estimate roughly the thermodynamic functions for the extraction of RuO$_4$ from nitric acid into CCl$_4$. From experiments at 0°C and 20°C the values $\Delta H = 2.1$ kcal/mole, $\Delta F = -2.0$ kcal/mole and $\Delta S = 15$ e.u./mole are found.

Finally activity coefficients of RuO$_4$ in saturated solutions have been obtained (Table 2) by extrapolation of the solubility data as a function of the square root of total concentration, $\sqrt{(C_s + S)}$ where S = solubility).

---

(9) W. F. McDEVIT and F. A. LONG, *Chem. Rev.* **51**, 119 (1952).

The absorption spectra of aqueous solutions of the orange red complexes at concentrations obeying Beer's law were taken by Hilger UVISPEK photoelectric spectrophotometer, model H700, with quartz dispersing prism and a 1 cm matched pair of quartz cells. In each spectrum, a broad absorption band of weak intensity with maxima at 380 (ϵ = 749), 372 (ϵ = 656), 378 (ϵ = 814) and 410 mμ[8] (ϵ = 652) was obtained for the peroxy group of the oxalato, maleato, malonato and sulphato complexes respectively.

Dissociation of the compounds in solution

The dissociation of the peroxy titanyl compounds in water can be expected to occur as follows

$$\mathrm{TiO_2X + H_2O \rightleftharpoons TiOX + H_2O_2} \tag{1}$$

$$\mathrm{TiO_2X + xH_2O \rightleftharpoons [TiO_2\,aq^{2+}] + X^{2-}} \tag{2}$$

where X is dicarboxylate or sulphate group. The dissociation according to the Equation (1) was investigated by the molar ratio method of HARVEY and MANNING[9], as given in Table 2. The dissociation according to Equation (2) was studied by the electrical conductivity of their aqueous solutions employing bright circular platinum electrodes set at 1 cm distance. In these experiments, the conductivity due to a small amount of H_2O_2 formed according to the Equation (1) was neglected, since its specific conductivity[10] is 2×10^{-6}. The *K* values found for the peroxy titanium compounds are oxalato = 1.32×10^{-3}, maleato = 1.88×10^{-3} and malonato = 2.56×10^{-3}. The conductivity for the sulphato complex could not be studied in water, since it hydrolysed giving rise to precipitates of hydrated titanyl peroxide.

TABLE 2.—DISSOCIATION CONSTANTS FOR THE PEROXY TITANYL GROUP OF COMPLEXES BY THE MOLAR RATIO METHOD

Peroxy titanyl complex	Concen (mole/l.) $\times 10^4$	Dissociation constant *K*
Oxalato	4.59	0.08×10^{-3}
Maleato	3.76	1.9×10^{-3}
Malonato	1.67	2.8×10^{-3}
Sulphato (in 1.5 N H_2SO_4)	3.25	6.4×10^{-3}

DISCUSSION

Nature and bonding of the peroxy group in peroxy titanium compounds. The nature of the peroxy group in titanium compounds can be understood from a knowledge of the stability and the nature of the peroxy group in hydrogen peroxide, dialkyl peroxides and alkali and alkaline earth metal peroxides. Hydrogen peroxide has a skew configuration,[11] which becomes less pronounced in dialkyl peroxides and tends to be linear with higher alkyl groups.[12] Thus, tertiary dibutyl peroxide has almost a linear configuration. All these compounds are quite stable at room temperature and do not give off oxygen under normal conditions. The alkali and alkaline earth metal peroxides are ionic in nature with O_2^{2-} ion in the solid state. The temperature of decomposition of the peroxy group of these peroxides is quite high(13) (> 450°C), compared to that of the peroxy titanium compounds,(14) which decompose around 100°C

---

[8] C. C. PATEL and M. S. MOHAN, *Nature, Lond.* **186**, 803 (1960).

[9] A. E. HARVEY and D. L. MANNING, *J. Amer. Chem. Soc.* **72**, 4488 (1950).

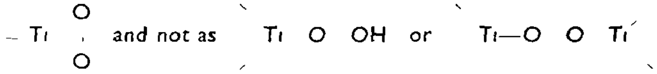
[10] A. C. CUTHBERTSON and O. MAASS, *J. Amer. Chem. Soc.* **52**, 489 (1930).

[11] S. C. ABRAHAMS, R. L. COLLIN and W. N. LIPSCOMB, *Acta Cryst.* **4**, 15 (1951).

[12] A. D. WALSH, *J. Chem. Soc.* 398 (1948).

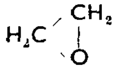
Alkali and alkaline earth metal peroxides give no infra-red absorption bands, attributable to the peroxide ion (15) Hydrogen peroxide in its vapour state also does not give any evidence for the O—O stretching frequency, but in its condensed state, it gives a weak band at about 880 cm^{-1} due to the O—O stretching vibration (16) Dialkyl peroxides also give a weak band in the region 830 890 cm $^{-1}$ due to the O—O vibration (17) On the other hand, peroxy titanium compounds give two bands around 1050 and 880 cm $^{-1}$, characteristic of the peroxy titanyl group These bands are absent in titanyl oxalate and titanyl hydroxide The occurrence and position of these two bands in peroxy titanium compounds indicate the absence of an ionic bond between titanium and the peroxy group and a non-linear nature of the peroxy titanyl group

The unstable nature of the peroxy group, the orange red colour of the compounds and the position of the two infra-red bands suggest that the peroxy group in the titanium compounds has neither the skew configuration of hydrogen peroxide nor the almost linear configuration of the higher dialkyl peroxides Their thermal instability suggests a strain in the peroxy group All these properties could be explained by representing the peroxy group by a ring configuration(18)



The skew configuration of hydrogen peroxide(12) is due to the electrostatic repulsion between the lone pairs of electrons, which are mutually perpendicular to each other on the O–O group In the ring structure, the O—O bond is twisted away from the stable skew configuration of hydrogen peroxide This will result in the lone pairs becoming nearly parallel and facing each other Such a configuration would cause increased electrostatic repulsion between the two oxygen atoms, resulting in a reduced overlap of the bonding orbitals of the O O group

Normally, titanium exhibits six co-ordinate valency, forming octahedral complexes with d^2sp^3 hybridization In the ring configuration, the O–Ti–O angle is expected to be about 90° and this should not change much The valence angle of each of the oxygens in the triangular configuration will then be about 45°, which is not feasible In general, the valence angle of oxygen ranges from 94 5° in trimethylene oxide to 124° in diphenyl ethers (19) Only in ethylene oxide,(19) which has a strained triangular



ring, the valence angle is 61 6° Thus the oxygen angles of the peroxy group cannot be as low as 45° To maintain a O–Ti–O angle of about 90° and also to satisfy the oxygen angles, one would expect a bent overlap of the bonding orbitals of the two oxygens, as represented below

---

(13) H Remy, *Treatise on Inorganic Chem* , Vol 1 (translated by J S Anderson) Elsevier, Amsterdam, (1956)

(14) G V Jere and C C Patel, *J Inorg Nucl Chem* **20**, 343 (1961)

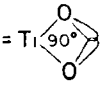
(15) E G Brame, S Cohen, L Margrave and V W Meloche, *J Inorg Nucl Chem* **4**, 90 (1957)

(16) R L Miller and D F Hornig, *J Chem Phys* **34**, 265 (1961)

(17) G J Minkoff, *Proc Roy Soc* **224** A, 176 (1954)

(18) C C Patel and G V Jere, Proceedings of 7th International Conference on Co-ordination Chemistry, Stockholm, 304 (1962)

(19) S C Abrahams, *Quart Rev* **10**, 407 (1956)



Such a configuration leads to reduced overlap of the bonding orbitals and consequent thermal instability of the O -O group

Colour and the electronic transitions in O –O group The orange red colour of the complexes is due to the peroxy titanyl group Since $(TiO_2)^{2+}$ has no *d* electrons, the colour of the compounds is not due to $d \leftrightarrow d$ transitions But the strong deformation of the coordinated O– O group postulated atoms might also lead to colour

The broad absorption bands in the region 370 to 410 mμ ($\epsilon \approx 700$) are due to the transitions of non-bonding electrons of the O O group to antibonding σ-orbitals(20) $(n \rightarrow \overset{\star}{\sigma})$ Such transitions are expected to be weak in intensity

The shift of the absorption maximum from 410 mμ in peroxy titanium sulphate to around 375 mμ in the dicarboxylato complexes may be due to a reduction in the strain of the non-bonding *p*-electrons in the O –O group This observation is supported by the greater stability of the peroxy group of the dicarboxylate complexes than that of the sulphato complex Among the dicarboxylato complexes, the shift of the absorption maximum is, however, not in the order of the stability of the dicarboxylate group of the complexes The same applies to the infra-red bands of the peroxy titanyl group The causes for these discrepancies are not clear

Relative stability of the peroxy and the dicarboxylate groups of peroxy titanium compounds The occurrence of the antisymmetrical stretching frequency of O—C—O group at 1715 cm^{-1} shows predominently covalent bonding(21,22) in the oxalato complex This character decreases in the order oxalato > maleato > malonato since the antisymmetrical stretching frequency progressively decreases while the symmetrical one increases (Table 1) This order is in agreement with the dissociation constants determined by the conductivity method

The decreasing order of stability of the peroxy group in peroxy titanium compounds is, in general oxalato > maleato malonato sulphato > peroxide

---

(20) S F Mason, *Quart Rev* **15**, 287 (1961)

(21) M J Schmelz, T Miyazawa, S Mizushima, T J Lane and J V Quagliano, *Spectrochim Acta* **9**, 51 (1957)

(22) J Fujita, K Nakamoto and M Kobayashi, *J Phys Chem* **61**, 1014 (1957)

J. inorg. nucl. Chem., 1963, Vol. 25, pp. 1161 to 1165. Pergamon Press Ltd. Printed in Northern Ireland

THE RATE OF AQUATION OF *TRANS*-CHLOROTHIOUREABIS (ETHYLENEDIAMINE) COBALT (III) CATION AND ANALOGOUS SUBSTITUTED THIOUREA COMPLEXES

W. A. BAKER, JR. and F. M. GAESSER
Department of Chemistry, Syracuse University, Syracuse 10, New York

(*Received* 18 *February* 1963, *in revised form* 21 *March* 1963)

Abstract—The kinetics of the aquation of $[Co(en)_2(tu)Cl]^{2+}$ (en = ethylenediamine, tu = thiourea) and some analogous substituted thiourea complexes have been studied at 25°C in 5×10^{-3} M nitric acid. The reactions are all first order in complex with rate constands varying from 2.0×10^{-5} to 3.2×10^{-3} sec^{-1}. Analysis of these spectra indicate little or no *trans* products. There was no evidence for a *trans* intermediate.

RECENTLY, INGOLD *et al.*[(1)] discussed the kinetics and mechanism of the replacement of Cl^- by H_2O in a series of complexes having the general form, *trans*-$[Co(en)_2ACl]^{2}$, where A = OH^-, N_3^-, Cl^-, NCS^-, NH_3, NO_2^-. From a consideration of the rate data as well as the steriochemical nature of the products they concluded that there was a duality of mechanisms operating, i.e., S_N1 and S_N2, and they further discussed various electronic effects which determine which of the two mechanisms predominates.[(2)] Thus, electron donating groups were interpreted as favouring an S_N1 mechanism and electron withdrawing groups an S_N2.

Since none of the complexes studied contained an orienting ligand (A) in which sulphur was attached to the metal, we thought it would be interesting to determine how the kinetics and nature of the products for such a complex compared with those previously reported. This is particularly so since BALDWIN[(3)] has observed that sulphite ion in a series of complexes *cis*-$[Co(en)_2SO_3X]$, has a strong labilizing effect on the X group and BABAEVA and BARANOVSKII[(4)] have noted the same effect in a number of cobalt-sulphite complexes. In these complexes the sulphite is known to bond through the sulphur, but in neither case are any rate data given.

In order to get quantitative data on a complex which we felt would have a Co–S bond, we chose to study *trans*-chlorothioureabis(ethylenediamine)cobalt (III) chloride. The results of this study, discussed later, led us to a similar consideration of a variety of analogous substituted thiourea complexes, since the spectra of the products indicated all or at least a very high proportion of *cis* product. It was felt that a study of a series of substituted thiourea complexes would assist in assigning a mechanism to the aquation reaction.

EXPERIMENTAL

Materials

Unless otherwise indicated, all chemicals employed in this work were reagent grade and used without further purification.

[(1)] C. K. INGOLD, R. S. NYHOLM and M. L. TOBE, *Nature, Lond.* **187**, 477 (1960).

[(2)] For a concise discussion of these and other results see, F. BASOLO and R. G. PEARSON, *Substitution Reactions of Metal Complexes. Advances in Inorganic Chemistry and Radiochemistry* Vol. 3, (Edited by H. J. EMELEUS and A. G. SHARPE) Academic Press, New York (1961).

[(3)] M. E. BALDWIN, *J. Chem. Soc.* 3123 (1961).

[(4)] A. V. BABAEVA and I. B. BARANOVSKII, *Russ. J. Inorg. Chem.*, 404 (1962).

$[Co(en)_2Cl_2]Cl$ was prepared by the method of BAILAR(5) and purified by the method of DAVIES.(6)

$[Co(en)_2tuCl]Cl_2$ was prepared by adding 0.76 g (1 × 10^{-2} moles) of thiourea to 3.0 g (1 × 10^{-2} moles) of *trans*-$[Co(en)_2Cl_2]$ in 200 ml of anhydrous methanol. An additional 400 ml of methanol was added and the solution allowed to stand at room temperature for three days. The solution was then reduced to approximately 60 ml in a rotating evaporator. After about two days, dull green crystals appeared which were filtered and washed with methanol and then ether. The crystals were pressed between filter papers and dried in a desiccator. (Found: S, 8.91; ionic Cl^-, 31.8; H, 5.7; C, 16.8. Calc. for $[Co(en)_2(CN_2H_4S)Cl]Cl_2$: S, 8.89; ionic Cl^-, 29.4; H, 5.5; C, 16.6%.)

All of the analogous substituted thiourea complexes were prepared in an identical manner, although in certain cases more extensive washing and recrystallization was necessary for purification. Composition was confirmed by analysis and the visible and ultra-violet spectra.

The fact that the complexes isolated were trans isomers is shown by the visible spectra, which show the splitting of the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition resulting in three peaks in the visible which is characteristic of the *trans* isomers of Co(III) complexes.(7) The values of λ_{max} for these three peaks are given in Table 1.

TABLE 1.—WAVELENGTH OF ABSORPTION MAXIMA FOR $[Co(en)_2ACl]^{2+}$ AND PRODUCTS OF THE AQUATION REACTIONS, $[Co(en)_2AH_2O]^{3+}$

	λ (mμ)	$[Co(en)_2ACl]^{2+}$		λ (mμ)	$[Co(en)_2AH_2O]^{3+}$
Chloride	612	450	400	512	370
Thiourea	615	455	408	515	373
N,N′-diethylthiourea	613	450	403	513	372
Allylthiourea	610	440	400	500	367
Ethylenethiourea	600	460	390	506	364
N,N′-di-2-tolythiourea	590	440	?*	—†	—†
Phenylthiourea	600	445	392	503	362

* Peak too broad to get accurate reading.

† Complex was too insoluble to determine kinetics under the same conditions as the others.

Kinetic measurements

Solutions of the complexes were prepared which were approximately 8.2 × 10^{-4} M in complex and 0.005 M in HNO_3. The complex was dissolved in solvent previously thermostated to 25 ± 0.2° and the reaction solutions were kept at the same temperature. Aliquots were taken at intervals for spectrophotometric measurements. The spectra were taken on a Perkin-Elmer 4000-A recording spectrophotometer over the range 350–750 mμ at 30 min intervals over a period of at least 4 hr.

In order to ascertain that thiourea was not released during the reaction, each complex was also studied in the ultra-violet region. In particular, the absorbance around 240 mμ was followed over a period of time equal to that for which the kinetic data were taken. In each case, there was no increase in absorbance at the wave length at which the free thiourea absorbs most strongly, indicating that at least over that period of time, thiourea was not released. The evidence indicates that at longer times (two days) some replacement occurs.

Treatment of data

First order plots of $\log (A_0 - A_\infty)/(A_t - A_\infty)$ vs t(8) were made for observed absorbances at approximately 600 and 500 mμ, the absorption maxima for reactants and products respectively. A_0

---

(5) J. C. BAILAR, JR., *Inorganic Synthesis* (Edited by W. C. FERNELIUS) Vol. 2, p. 222. McGraw-Hill, New York (1946).

(6) E. W. DAVIES, *J. Phys. Chem.* **65**, 1328 (1961).

(7) R. G. WILKINS and M. J. G. WILLIAMS, *Modern Co-ordination Chemistry* (Edited by J. LEWIS and R. G. WILKINS) pp. 188–190. Interscience, New York (1960).

(8) A. A. FROST and R. G. PEARSON, *Kinetics and Mechanisms* p. 37. J. Wiley, New York (1953).

was obtained by plotting A_t vs t and extrapolating to time zero Excellent agreement was obtained for A_0 from different kinetic runs A_∞ was obtained from the spectra after approximately 48 hr In all cases, the log plots gave very nice straight lines from which the rate constants were obtained At least three kinetic runs were made for each complex and good agreement between rate constants was observed

Infra-red measurements

All infra-red spectra were taken on a Perkin–Elmer Infracord using the KBr wafer technique

RESULTS AND DISCUSSION

Since it is known that thiourea co-ordinates to a large number of metal ions, e g , Cu(I), Ni(II), Co(II), and Mn(II),(9,10) through the sulphur, we felt reasonably certain that it was sulphur-bonded in our complexes Since the possibility of coordination through the nitrogen also exists, we made a cursory infra-red study in an effort to obtain confirmatory evidence to support our belief Unfortunately, the results were not conclusive BELLAMY(11) reports that the C=S frequency in thioureas falls in the range of 1408–1150 cm^{-1} In all of the thioureas that we studied there is a band in the region of 1430–1400 cm^{-1} which apparently shifts slightly to longer wavelengths to around 1390–1360 cm^{-1} in the complexes Unfortunately, ethylenediamine also absorbs in the region around 1350 cm^{-1} so the spectra of the complexes is not unambiguous There is also a band in all of the thioureas which falls in the region of 1550–1500 cm^{-1} This disappears completely in the complex GREGG(12) has stated that such a frequency is characteristic of C=S groups, although this does not seem to be substantiated by other workers (11) The results of our work do not therefore, prove the conclusion that the thiourea is bonded through the sulphur Presumably a more sophisticated study, which ours was certainly not, would settle this point On the basis of the evidence available, we do believe that this is the case

The rate constants for the aquation reaction

$$[\mathrm{Co(en)_2(X\text{–}tu)Cl}]^{2+} + \mathrm{H_2O} \rightarrow [\mathrm{CO(en)_2(X\text{-}tu)H_2O}]^{3+} + \mathrm{Cl}^-$$

are given in Table 2 Our value for $[\mathrm{Co(en)_2Cl_2}]^+$ as well as that of PEARSON *et al* (13) are given for comparison along with values for other complexes of similar type The rate constants alone are not diagnostic of the mechanism of reaction, since the values observed for the thiourea complexes are of the same order of magnitude as those for the case A—NH_3 and A=Cl^-, which have been postulated by INGOLD *et al*, to undergo aquation by different mechanisms (1) Whatever the mechanism it is obvious that thiourea has no drastic effect on the rate of aquation

It is interesting to note, nevertheless, that phenyl substitution increases the rate while all others decrease the rate relative to unsubstituted thiourea, and that among the substituents studied, phenyl is the only electron withdrawing group All of the others are, relative to hydrogen, electron donating (14) Such a result might tend to

---

(9) C B KNOBLER, Y OKAYA and R PEPINSKY *Z Krist* **111**, 385 (1959)

(10) M NARDELLI, L CAVALCA and A BRAIBANTI, *Gazzetta*, **86**, 867 (1956) **87**, 917 (1957)

(11) L J BELLAMY, *The Infra-red Spectra of Complex Molecules* pp 355 357 J Wiley New York (1958)

(12) E C GREGG, JR , *J Amer Chem Soc* **74**, 3691 (1952)

(13) R G PEARSON, R E MEEKER and F BASOLO, *J Amer Chem Soc* **78**, 2673 (1956)

(14) R W TAFT, JR , *Steric Effects in Organic Chemistry* (Edited by M S NEWMAN) Chapter 13 J Wiley, New York (1956)

argue for an S_N2 mechanism [1] However, a consideration of the relative inductive effects[14] of the compounds studied predicts, on this basis, the order tu > allyl-tu > ethylene-tu > diethyl-tu for the rate constants This order is not in accord, as can be seen from Table 2, with the observed rates In addition, BASOLO, *et al* [15] found in a study of the inductive effect in substituted pyridines that such substitution has only a very small effect on the rate, and reasoning indicates even less an effect in our compounds It seems reasonable to conclude, therefore, that the rate constants are not necessarily indicative of the mechanisms

TABLE 2 —RATE CONSTANTS FOR THE AQUATION OF $[Co(en)_2ACl]^{2+}$ AT 25

A	k (sec^{-1}) 10^{5}
OH	140*
N_3	25*
Cl	1 6* †
NCS	0 005*
NH_3	4*
NO_2	98*
Cl	1 8† ‡
tu	2 9‡
Ethylene-tu	2 5‡
Allyl-tu	2 0‡
Phenyl-tu	3 2‡
N N′-diethyl-tu	2 8‡

* Taken from reference (1)

† One-half the observed rate, i e , value for one chloride

‡ Our data

The sterochemical nature of the products is often a great aid in establishing a mechanism Study of the spectra of the thiourea complexes revealed a number of important facts

(1) The relative amounts of *cis* and *trans* products remain constant over a period of at least four half-lives of the reactions This is shown by the fact that all the spectra for a given reaction over this period of time have several common crossing points which do not change with time and also by the fact that the rate constants derived from the decrease in absorbance at approximately 610 mμ agree, over the full course of the reaction, with that obtained from the increase in intensity of the product peak around 510 mμ.

(2) The amount of *trans* product present after long times is at most very small We were not able to use the very nice method utilized by INGOLD *et al* [16] for a precise evaluation of the product composition because we have been unable to prepare the pure *cis*- and *trans*-$[Co(en)_2(tu)H_2O]^{3+}$ complexes However, inspection of the spectra after four half-lives of the reaction shows no detectable trace of *trans* product The *trans* isomer would be expected to show a strong peak shifted slightly to shorter wavelengths relative to the starting complex Since the 610 mμ peak of the reactant

[15] F BASOLO, J G BERGMANN, R E MEEKER and R G PEARSON, *J Amer Chem Soc* **78**, 2676 (1956)

[16] C K INGOLD, R S NYHOLM and M L TOBE, *J Chem Soc* 1691 (1956)

is still detectable (but barely) after three half-lives (87 per cent completion), it seems reasonable to assume that the product is *at least* 80 per cent *cis*. These two items suggest that the *cis* isomer is the primary if not the only product of the aquation reaction.

There are two reasonable mechanisms that would yield a product that was primarily *cis*. An S_N2, *trans* attack would be expected to yield 100 per cent of the *cis* isomer while an S_N1 mechanism going through a trigonal bipyramid intermediate would be predicted to yield 67 per cent *cis* on purely statistical grounds, but higher percentages are certainly reasonable.(17)

A consideration of the data in Table 2 would seem to rule out the S_N2 mechanism, since substitution on thiourea would sterically hinder an incoming group and appreciable decrease the rate of reaction. As is indicated in Table 2, the phenyl substituted complex actually reacts faster than the unsubstituted and in the other cases where slower rates are observed, the decrease is small. Although it is not possible to quantitatively evaluate the expected change in rates, it seems reasonable that if the mechanism was primarily an S_N2 *trans* attack, larger effects than those observed should be expected.

In view of the above facts, we feel that the most logical mechanism is an S_N1 with a trigonal bipyramid intermediate. Such a mechanism would be expected to yield some *trans* product with the per cent *trans* dependent upon the nature of the substituted thiourea. In general, the bulkier the thiourea derivative, the greater the amount of *trans*.(17) As previously stated, since we have not been able to prepare the pure aquo products, we have not been able to investigate this possibility.

The relative values of the rate constants observed for the substituted thiourea is not directly interpretable in any simple terms. It would be expected that in the S_N1 as in the S_N2 mechanism, steric effects would influence the observed rates, and on this basis alone, the increased rate for the phenyl derivative is unusual. However, the observed rates, being so nearly the same, are obviously a result of both electronic and steric factors so lack of direct correlation with either is not unexpected.

Finally, it should be pointed out that there is one condition under which any conclusion based on our data would be invalid. That is, if the rates of isomerization of the products of the aquation are very fast compared to the rate of aquation, then our data could be obtained by either an S_N1 or an S_N2 mechanism, since under these conditions, the sterochemical nature of the products would have no bearing on the mechanism of aquation. For obvious reasons, we are unable to evaluate the rate of isomerization.

---

(17) F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions* pp. 215-222. J. Wiley, New York (1958).

J. Inorg. Nucl. Chem. 1963. Vol. 25, pp. 109 to 115. Pergamon Press Ltd. Printed in Northern Ireland

THE EXTRACTION OF URANIUM (VI) FROM NITRIC ACID SOLUTIONS BY DI-(2-ETHYLHEXYL)-PHOSPHORIC ACID

TAICHI SATO
Government Chemical Industrial Research Institute,
Honmachi, Shibuya-ku, Tokyo, Japan

(*Received* 5 *March* 1962; *in revised form* 4 *July* 1962)

Abstract—The partition of uranium (VI) between nitric acid solutions and solutions of di-(2-ethylhexyl)-phosphoric acid (DEHPA) in kerosene have been investigated under varying conditions. Changes in acidity of the organic solutions have been measured and infra-red spectra of the organic phases obtained. The mechanism of extraction is discussed in the light of the results obtained.

THE extraction of uranium (VI) from sulphuric acid solutions by di-(2-ethylhexyl)-phosphoric acid (DEHPA) has been described in a previous paper,[1] and the present study concerns the mechanism of extraction from nitric acid solutions.

EXPERIMENTAL

DEHPA (Virginia Carolina Chemical Corporation) was purified as described previously.[1] Extractions were carried out by shaking equal volumes (20 ml) of DEHPA diluted with kerosene and uranyl nitrate solution containing nitric acid in a 50 ml stoppered conical flask at the required temperature. Preliminary experiments showed that equilibration was complete in 5 min. Uranium extracted into the organic phase was back-extracted with 6 N hydrochloric acid solution, and the partition coefficient was determined as the ratio of the equilibrium concentrations in the organic and aqueous phases. Uranium was determined by EDTA titration using xylenol orange as indicator.[2]

The acidity of the organic phase were determined by adding 2 ml to 25 ml of 75 per cent ethyl alcohol containing 2 per cent sodium oxalate solution and titrating with 0.03 N sodium hydroxide solution using phenolphthalein as indicator.

Infra-red spectra were obtained as previously described.[1]

RESULTS AND DISCUSSION

(a) *Dependence on acid and solvent concentration*

Fig. 1 shows that the partition coefficient for extraction of uranium (VI) into DEHPA from nitric acid solutions decreases with increasing acidity below 3 M; above this acidity the curve is similar to that obtained with tri-n-butyl phosphate (TBP),[3] the partition coefficient increasing with acidity up to 6 M and then decreasing again at higher acidities. For the similar pattern shown by di-n-butyl phosphoric acid HARDY[4] and others[5] have suggested that at low acidities uranium is extracted by a cation-exchange reaction in which hydrogen ion is liberated and at higher activities by a reaction similar to that with non-ionic reagents.

---

[1] T. SATO, *J. Inorg. Nucl. Chem.* **24**, 699 (1962).

[2] J. KINNUNEN and B. WENNERSTRAND, *Chemist-Analyst* **46**, 92 (1957).

[3] E.g., K. ALCOCK, G. F. BEST, E. HESFORD and H. A. C. MCKAY, *J. Inorg. Nucl. Chem.* **6**, 328 (1958).

[4] C. J. HARDY, AERE Report R-3267 (1959), *J. Inorg. Nucl. Chem.* **21**, 348 (1961).

[5] T. V. HEALY and J. KENNEDY, *J. Inorg. Nucl. Chem.* **10**, 128 (1959).

J Inorg Nucl Chem 1963, Vol 25 pp 1167 to 1173 Pergamon Press Ltd Printed in Northern Ireland

NATURE OF THE HYDROGEN ION EFFECT ON THE EXTRACTION OF Co(II) FROM AQUEOUS CHLORIDE MEDIA BY SUBSTITUTED AMMONIUM CHLORIDES OF HIGH MOLECULAR WEIGHT

M L Good, S E Bryan, F F Holland, Jr and G J Mals
Department of Chemistry, Louisiana State University New Orleans

(*Received* 17 *December* 1962, *in revised form* 27 *March* 1963)

Abstract—The phenomena associated with the decreased extraction of certain metals [particularly Co(II)] from concentrated HCl solutions by organic solutions of high molecular weight, substituted ammonium chlorides has been investigated The spectra of the metal species in both the aqueous and organic phases for both LiCl and HCl systems have been determined, indicating no spectral differences in the species extracted from the two systems The extraction process has been studied as a function of the HCl concentration and infrared spectra of the organic phase containing extracted HCl have been obtained Extraction isotherms for the extraction of the metal ion from 12 M HCl and 12 M LiCl have been compared The results show that at high aqueous HCl concentration, the substituted ammonium chloride solutions extract excess HCl, probably in the form of the hydrogen dichloride ion with excess hydrogen-bonded molecular HCl A possible conclusion from this study is that the exchange equilibrium for the extraction of the cobalt anion is displaced by the reaction of the substituted ammonium chloride with the excess HCl, thus reducing the extractability of the metal

Previous studies on the extraction and ion exchange behavior of metals which form complex chloride anions in hydrochloric acid solutions have shown that extraction and adsorption curves of certain metals exhibit maxima at high acid concentrations (1–4) This phenomena is particularly noticeable for divalent cations such as Co(II), Zn(II), Cu(II) and Mn(II) Also we have observed this effect in In(III) solutions where the extracting species is believed to be $InCl_5^{2-}$ (5) In an effort to elucidate the mechanism involved in this decreased extraction at high HCl concentrations a study of the Co(II)-chloride system versus organic solutions of high molecular weight, substituted ammonium chlorides was undertaken It has been shown rather conclusively that these compounds behave essentially as liquid anion exchangers, therefore information which applies to their behavior should, in general, be applicable to solid state anion exchange resins (3,4,6) This paper describes and compares the extraction of Co(II) from LiCl and HCl systems by several liquid anion exchangers

---

(1) K A Kraus and F Nelson, *The structure of Electrolytic Solutions* pp 340–364 and the earlier literature cited therein (Edited by W J Hamer) J Wiley, New York (1959)

(2) H A Mahlman, G W Leddicotte and F L Moore, *Analyt Chem* **26**, 1939 (1954)

(3) M L Good and S E Bryan, *J Inorg Nucl Chem* **20**, 140 (1961)

(4) A M Wilson, L Churchill, K Kiluk and P Hovsepian, *Analyt Chem* **34**, 203 (1962)

(5) *J Inorg Nucl Chem* In press

(6) F L Moore, National Academy of Sciences National Research Council, Document No 3101 December 1960 and the earlier literature cited therein

EXPERIMENTAL

Materials The amines or amine salts used were the following tri-n-hexyl amine—Eastman Kodak white label, 2 2-diethyldihexylamine Eastman Kodak yellow label, tricaprylyl monomethyl ammonium chloride General Mills commercial compound (marketed as Aliquat 336), tri-n-octylamine General Mills commercial compound (marketed as Alamine 336), and triisooctylamine Gulf Research development chemical All of these materials were used without subsequent purification All other materials were usual stock items of Reagent Grade quality

Procedures All extraction data were obtained using a tracer technique reported previously (4) In all cases reported, good phase separation after equilibrium was obtained and no significant changes of phase volume occurred

Standardization of the organic amine solutions and determination of HCl in the organic phases was done by a non-aqueous titration method using a standard benzene methanol solution of sodium methoxide with thymol blue as an indicator (7) One or two endpoints for the thymol blue were obtained depending on whether excess HCl (that necessary to form the hydrochloride plus more) was present or not A red to yellow endpoint was followed by a yellow to blue endpoint if excess HCl were present Both endpoints were sharp and reproducible Potentiometric curves were obtained and the colour changes were found to correspond to the neutralization of the excess HCl (red to yellow) and the neutralization of the hydrochloride of the amine (yellow to blue) The difference of the titers of the two equivalence points gives the concentration of the amine itself The titer of the first equivalence point gives the concentration of the excess HCl in the organic solution This same non-aqueous titration has been reported by BERTOCCI and ROLANDI(8) and their results on amine HCl solutions are completely in agreement with ours

Spectra All visible spectra reported were obtained using 1 cm silica cells (in some cases the path length was reduced by inserting 9 mm silica spacers) in a Beckman Model DK-1 or a Model DU Spectrophotometer All extinction coefficient data was calculated from absorbance measurements obtained on the Model DU

The infra-red spectra were first obtained on a Beckman Model IR-5 and then repeated on a Beckman Model IR-7 Sodium chloride cells were used in all cases

RESULTS AND DISCUSSION

Several extractions of Co(II) as a function of the chloride ion concentration were carried out Representative curves are shown in Fig 1 It can be seen here that the percent extraction from HCl solutions does not approach very closely to 100 per cent, even for those amine hydrochlorides or quaternary salts which show exceptionally good extraction properties for complex chloride anions In contrast the extraction from LiCl solutions is essentially 100 per cent for the tertiary amines and the quaternary salts and approaches 100 per cent even for a secondary amine hydrochloride which has been shown to be a poor extractant for complex chloride anions (1 9) Further evidence of the effect of HCl on the extraction of Co(II) is shown in Fig 2 As the fraction of HCl becomes appreciable with respect to the LiCl concentration, the extraction of the Co(II) decreases although the total chloride ion concentration remains unchanged

A spectral study of both the aqueous and organic phases of the extraction system was undertaken to ascertain the Co(II) species present in each case Apparent extinction coefficients were calculated at the absorbance maxima assuming that all of the Co(II) was contained in the species contributing to the particular absorbance peak The results of this study are shown in Fig 3 and Table 1 The spectra shown in Fig 3 indicate that the principal species presence in 12 M LiCl, in 12 M HCl and

---

(7) J S FRITZ and N M LISICKI, *Analyt Chem* **23**, 589 (1951)

(8) U BERTOCCI and G ROLANDI, *J Inorg Nucl Chem* **23**, 323 (1961)

(9) M L GOOD and S E BRYAN, *J Amer Chem Soc* **82**, 5636 (1960)

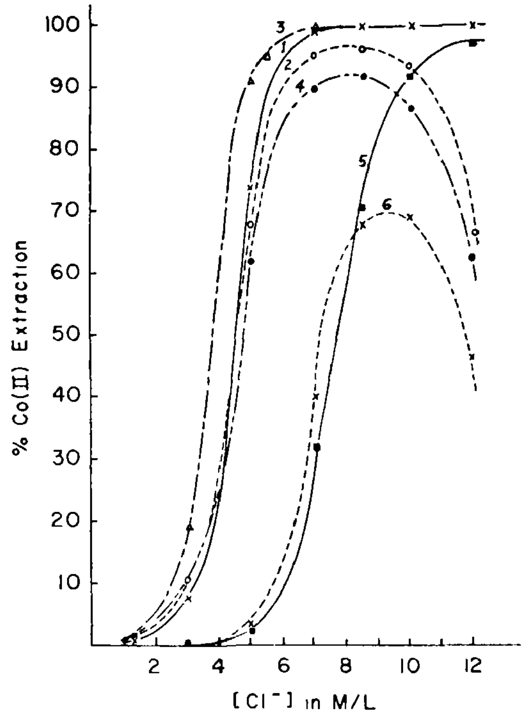


FIG. 1.—Extraction of Co(II) from Cl^- solutions ([Co(II)] was 0.025 M). Curve 1—0.020 M tri-n-hexyl amine in toluene vs LiCl. Curve 2—same as Curve 1 vs HCl, Curve 3—0.176 M tricaprylmonomethyl ammonium chloride in toluene vs LiCl, Curve 4—same as Curve 3 vs HCl, Curve 5—0.20 M 2,2-diethyldihexyl amine in toluene vs LiCl, Curve 6—same as Curve 5 vs HCl

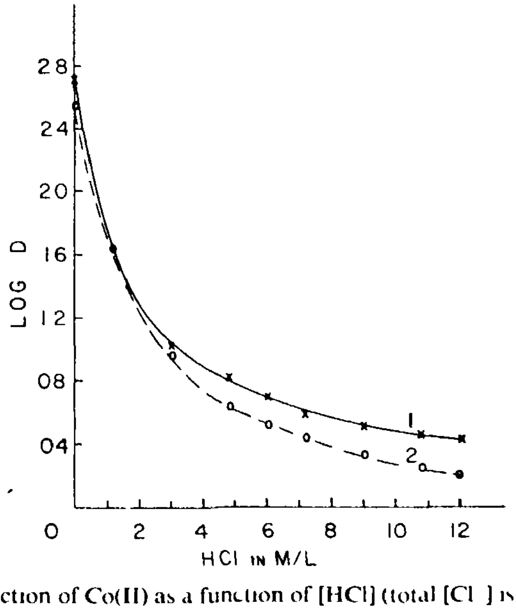


FIG. 2.—Extraction of Co(II) as a function of [HCl] (total [Cl^-] is 12 M and [Co(II)] is 0.025 M). Curve 1—0.200 M tri-n-hexyl amine in toluene, Curve 2—0.176 M tricaprylmonomethyl ammonium chloride in toluene

the extracted organic phase are all the same. This characteristic spectra has been attributed to the tetrahedral $CoCl_4^{2-}$ by several investigators.[(10, 11, 12)] The apparent extinction coefficient values as tabulated in Table 1, indicate that the concentration of $CoCl_4^{2-}$ in a 8.5 M HCl solution is significantly higher than in an 8.5 M LiCl solution, but at 12 M Cl⁻ (whether all HCl or LiCl or a mixture of the two) the contribution to the spectra from this ion seems to be essentially the same. The

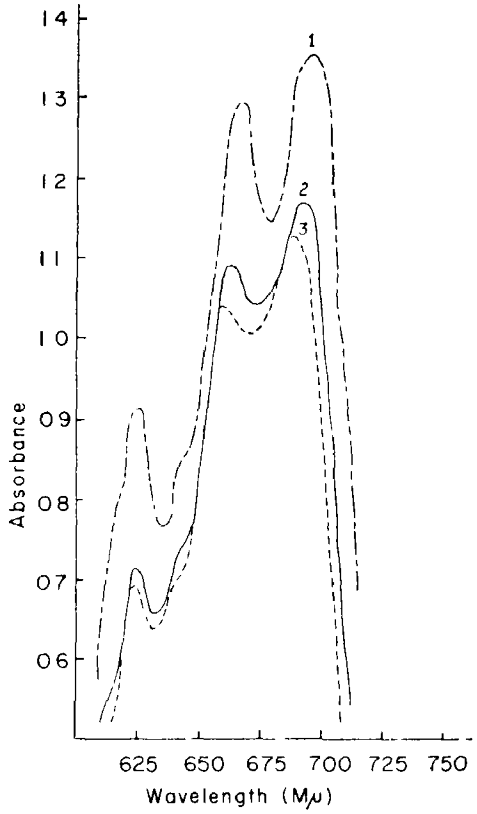


FIG. 3.—Spectra of various Co(II) solutions. Curve 1—0.0249 M Co(II) in 0.2 M tri-iso-octyl amine in toluene (0.1 cm path length); Curve 2—0.00202 M Co(II) in 12 M HCl; Curve 3—0.00199 M Co(II) in 12 M LiCl (0.25 M HCl).

extinction coefficient values vary slightly with Co(II) concentration which would indicate that some small fraction of the Co(II) is not present as $CoCl_4^{2-}$. This would be consistent with some recent work by COTTON *et al.*[(13)] which indicates that complete conversion of the Co(II) to $CoCl_4^{2-}$ does not occur in either 12 M HCl or 12 M LiCl. However, if one assumes that the extracted species in the organic–amine layer is $CoCl_4^{2-}$ (and this seems reasonable from the spectra and from extraction isotherms[(3)]) the Co(II) in the aqueous phase at 12 M Cl⁻ must be almost completely $CoCl_4^{2-}$. In any case the spectral data indicate that the Co(II) species involved in the extraction

[(10)] L. I. KATZIN and E. GEBERT, *J. Amer. Chem. Soc.* **72**, 5464 (1950).

[(11)] N. S. GILL and R. S. NYHOLM, *J. Chem. Soc.*, 3997 (1959).

[(12)] D. A. FINE, *J. Amer. Chem. Soc.* **84**, 1139 (1962).

[(13)] F. A. COTTON, D. M. L. GOODGAME and M. GOODGAME, *J. Amer. Chem. Soc.* **83**, 4690 (1961).

is the same for HCl and LiCl solutions, thus the decrease in extractability of the Co(II) at HCl concentrations above 9 M is not due to the formation of an unextractable Co(II) species (unless the unextractable species has the same spectra as that of the extractable species)

To further investigate the differences in the extraction from HCl and LiCl solutions, several solutions containing only HCl or LiCl (with 0 25 M HCl) were extracted with the organic-amine solutions The only material extracted from the LiCl solutions was a small amount of HCl corresponding to the formation of the amine hydrochloride The quaternary salt extracted no detectable amount of HCl or LiCl from the aqueous solution The results of the HCl extraction are given in Table 2 The extraction of Co(II) from comparable solutions is shown for comparison purposes In the cases of the two amines, the extracted HCl concentration as shown in Table 2 is the acid in excess of the amount required to form the hydrochloride As can be seen the amount of excess HCl absorbed in the organic phase increases steadily with increasing HCl concentration The actual quantity of absorbed HCl is much greater in the case of the quaternary salt than in the case of the amines This corresponds to the poorer extraction of Co(II) from HCl solutions by this quaternary salt as compared to the amines Since the quaternary salt appears to be the best extractant for Co(II) from LiCl solutions (see Fig 1) it would appear that the decreased extraction from the HCl solutions is due to the excess HCl which extracts into the organic phase Apparently if the tendency to extract excess HCl is high, this reaction competes with the $CoCl_4^{2-}$ ion-exchange reaction thus decreasing the overall Co(II) extraction

TABLE 1 --SPECTRAL DATA FOR VARIOUS Co(II) SOLUTIONS

Solution composition	λ_{max} (mμ)	$-\epsilon_{max}$	λ_{max} (mμ)	$-\epsilon_{max}$	λ_{max} (mμ)	$-\epsilon_{max}$
0 00250 M Co^{2+} in 8 5 M HCl	690	352	665	332	625	226
0 00125 M Co^{2+} in 8 5 M HCl	690	360	665	336	625	228
0 00256 M Co^{2+} in 8 5 M LiCl	690	268	665	248	625	170
0 00202 M Co^{2+} in 12 M HCl	687	550	662	521	622	352
0 001992 M Co^{2+} in 12 M LiCl (0 25 M HCl)	687	552	662	515	622	351
0 0249 M Co^{2+} in 12 M LiCl (0 25 M HCl)	687	534	662	502	622	341
0 00200 M Co^{2+} in 6 M LiCl + 6 M HCl	687	562	660	530	622	360
0 00200 M Co^{2+} in 3 M LiCl + 9 M HCl	687	550	660	520	622	350
0 00200 M Co^{2+} in 9 M LiCl + 3 M HCl	687	575	662	537	622	365
0 0249 M Co^{2+} in 0 2 M triisooctyl amine in trichloroethylene (extracted from 12 M LiCl)	695	542	665	506	625	365
0 0024 M Co^{2+} in 0 02 M tri-n-hexyl amine in C_6H_6 (extracted from 8 5 M HCl)	700	583	665	571	630	408
0 00227 M Co^{2+} in 0 02 M tri-n-hexyl amine in trichloroethylene (extracted from 8 5 M HCl)	695	549	665	535	630	372
0 0016 M Co^{2+} in 0 05 M tri-n-hexyl amine in $CHCl_3$ (extracted from 8 5 M HCl)	695	586	665	555	625	388

The nature of the HCl in the organic phase deserves some consideration By what mechanism does the amine hydrochloride or the quaternary salt extract this HCl?

In some previous work on HCl solutions of halide salts of organo-nitrogen bases, it has been suggested that the formation of the hydrogen dichloride ion (HCl_2) occurs Infra-red spectra of solutions containing HCl and these halide salts were used to identify the species and a characteristic absorption at 1180 cm ^{1} was assigned to the ion HCl_2 (11 17) Several infra-red spectra of our organic phases containing either the quaternary salt or the amine hydrochloride and excess HCl were obtained In all cases a broad characteristic absorption peak of high intensity between 1110 and 1210 cm^{-1} with a maximum at 1170 cm^{-1} was obtained Similar spectra of solutions of the same salts without excess HCl showed no or insignificant absorption in this region Thus it would appear that these solutions have absorbed the HCl in the organic phase as HCl_2^- However, it is true that more HCl is absorbed (particularly in the case of the quaternary salt) than can be accounted for by the formation of one HCl_2^- per salt molecule (see Table 2) Thus some excess molecular HCl must be present, probably hydrogen-bonded to the HCl_2^- Unfortunately the characteristic infra-red band for HCl at 2840 cm^{-1} would be completely masked by the C—H stretching frequency of the amines and no spectral evidence can be presented for the existence of this molecule in the organic phase

TABLE 2 COMPARISON OF Co(II) EXTRACTION WITH CONC OF HCl IN ORGANIC PHASE

	0 176 M tri-capryl mono-methyl ammonium chloride in toluene		0 158 M tri-n-octyl amine in toluene		0 200 M tri-n-hexyl amine in toluene	
Conc of HCl in aq soln (M)	Distribution coefficient *D**	Conc of excess HCl† (M)	Distribution coefficient *D*	Conc of excess HCl† (M)	Distribution coefficient *D*	Conc of excess HCl† (M)
6 0	3 14	0 170	4 51	0 047	5 97	0 066
6 5	4 69	0 188	8 06	0 064	8 57	0 080
7 0	7 11	0 023	12 7	0 078	13 4	0 097
7 5	9 35	0 218	18 9	0 092	19 8	0 109
8 0	11 3	0 232	22 7	0 110	20 1	0 120
8 5	10 9	0 245	25 2	0 124	26 4	0 139
9 0	10 7	0 259	20 7	0 141	26 3	0 152
9 5	8 77	0 272	18 2	0 159	20 0	0 171
10 0	6 75	0 286	12 1	0 175	14 1	0 181
10 5	5 34	0 296	9 02	0 188	10 3	0 191
11 0	3 87	0 317	5 10	0 213	5 80	0 208
11 5	2 88	0 316	3 78	0 221	4 09	0 211
12 0	2 01	0 343	2 27	0 249	2 70	0 228

* Total Co(II) conc was 0 025 M *D* $[Co(II)]_{org}/[Co(II)]_{aq}$ act (cm)$_{org}$/act (cm)$_{aq}$

† These values are corrected for the amount of HCl which extracts into toluene when the amine is not present All values are for the extraction of HCl from an aqueous solution containing no cobalt

The most reasonable conclusion from this study seems to be that excess HCl in the aqueous phase complicates the extraction process by competing with the exchange

---

(14) D Herbrandson and J Weinstein, *J Amer Chem Soc* **76**, 4046 (1954)

(15) T C Waddington, *J Chem Soc* , 1708 (1958)

(16) Y Pocker, *J Chem Soc* , 1292 (1962)

(17) W Gerrard and H R Hudson, *Proc Chem Soc* 467 (1961)

reactions as shown below

$$2R_3NH^+Cl^- \ (org) + CoCl_4^{2-} \ (aq) \rightleftharpoons (R_3NH^+)_2CoCl_4^{2-} \ (org) + 2Cl^- \ (aq) \quad (1)$$

$$R_3NH^+Cl^- \ (org) + HCl \ (aq) \quad R_3NH^+HCl_2^- \ (org) \quad (2)$$

That such a competition reaction is involved is borne out by the extraction isotherms shown in Fig 4 The amine-hydrochloride or the quaternary salt loads at 2 1 with respect to Co(II) when the solution extracted contains 12 M LiCl even at low total Co(II) concentrations However, if 12 M HCl solutions are used this ultimate loading of 2 1 is approached only as the Co(II) concentration is increased to quite high levels

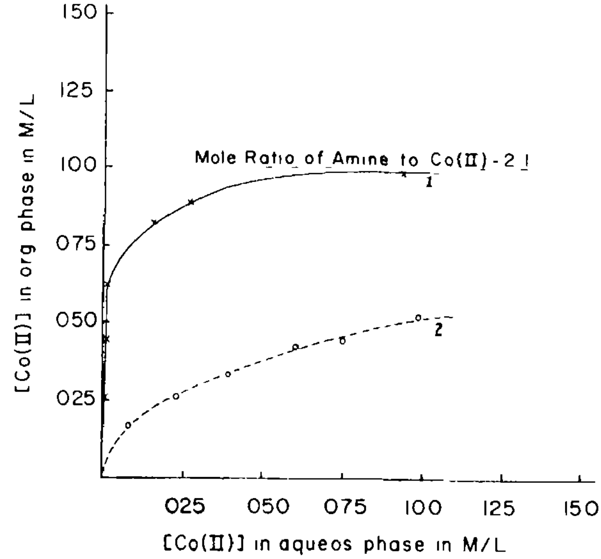


FIG 4—Extraction isotherms for Co(II) by 0 200 M tri-n-hexyl amine in toluene (equilibrium concentrations of Co(II) in the aqueous phase vs those in the organic phase), Curve 1—aqueous solution is 12 M LiCl (0 25 M HCl), Curve 2—aqueous solution is 12 M HCl

It should be pointed out that this study does not eliminate the possibility of the formation of $HCoCl_4^-$ or H_2CoCl_4 in the solutions containing high HCl concentrations, provided the spectra of these acid species are essentially the same as that for $CoCl_4^{2-}$ The formation of these species could account for the decreased extractability from HCl solutions as compared to LiCl solutions However if this were the cause of the decreased extraction one might expect the decrease in the extraction efficiency of the quaternary salt to be the same as that for the amine hydrochloride Since this is not the case and the greater effect is shown by the quaternary salt which extracts more excess HCl, it would appear that this excess HCl must be involved in the process which decreases the extraction However, it is certainly possible that some combination of these two phenomena may be instrumental in the decreased extraction of Co(II) from highly concentrated HCl solutions by quaternary salts and amine hydrochlorides

Acknowledgements—We would like to thank MR D BOSTICK and MR M VILLARREJOS for their assistance with some of the experimental work We would also like to thank General Mills and Gulf Research for their contributions of some of the liquid anion exchangers

A major part of this investigation has been supported by the United States Atomic Energy Commission under contract No AT-(40-1)-2576

J Inorg Nucl Chem, 1963 Vol 25 pp 1175 to 1189 Pergamon Press Ltd Printed in Northern Ireland

APPLICABILITY OF CERTAIN ORGANO PHOSPHORUS EXTRACTANTS TO ENVIRONMENTAL AND BIOLOGICAL RADIOACTIVITY SURVEYS*

D F Peppard, G W Mason and C M Andrejasich
Argonne National Laboratory, Argonne, Illinois

(*Received* 18 *January* 1963, *in revised form* 22 *February* 1963)

Abstract—The applicability of certain organo phosphorus extractants to environmental and biological radioactivity surveys has been demonstrated Specifically, a solution of mono 2-ethyl hexyl phosphoric acid, H_2MEHP, in a hydrocarbon and/or chlorinated hydrocarbon diluent has been shown to extract radioactive Ce(III), Pm(III), Y(III), Am(III), Pu(III), Th(IV), Np(IV), Pu(IV) and U(VI) from acidified human urine with sufficiently high K values to permit basing a scheme of analysis for such radioelements upon liquid–liquid extraction

The specific K value is strongly dependent upon the valence of the element, permitting a partial mutual separation of the above set of elements through use of the H_2MEHP (hydrocarbon and/or chlorinated hydrocarbon) vs HCl system These separation possibilities are multiplied by introduction of negative synergist, specifically 2-ethyl hexanol-1, which serves to progressively inactivate H_2MEHP Consequently, under certain conditions, M(III) may be scrubbed from an extract leaving M(IV) and M(VI) in the organic phase, but under another set of conditions involving a greater relative concentration of negative synergist, M(VI) may be scrubbed from the extract leaving M(IV) in the organic phase Further mutual separation is accomplished by means of extraction with di 2-ethyl hexyl phosphoric acid, HDEHP, this extractant serving to separate Y from Pm Ce(III) and Am and to separate Ce(IV) from Pm and Am Finally, extraction with tri n-octyl phosphine oxide, TOPO, is utilized in the separation of U(VI) from Pu(III)

Through use of selected diluents of different densities, the organic phase has been made the upper or lower phase in accordance with maximum ease of manipulation

Flow sheets have been devised and tested Advantages of the techniques are discussed, and other areas of application are suggested

One of the attractive features of liquid–liquid extraction systems involving acidic organo phosphorus esters as extractants is the fact that many of the metals pertinent to environmental radioactivity surveys may be extracted quite efficiently despite the presence of a mineral acid in appreciable concentration in the aqueous phase The reported studies of types of extractants include $(GO)PO(OH)_2$,(1) $(GO)_2PO(OH)$,(2) both (GO)PO(OH)$_2$ and (GO)$_2$PO(OH),(3) separately and in admixture, (GO)G′PO(OH),(4) and (G)$_2$PO(OH),(3b 3c) where G and G′ are organic groups

---

* Based on work performed under the auspices of the U S Atomic Energy Commission

(1) (a) D F Peppard, G W Mason and R J Sironen *J Inorg Nucl Chem* **10**, 117 (1959)
(b) C G Warren and J F Suttle, *J Inorg Nucl Chem* **12**, 336 (1960)
(c) G W Mason, S McCarty and D F Peppard, *J Inorg Nucl Chem* **24**, 967 (1962)
(d) R D Baybarz and R F Leuze, *Nucl Science and Engng* **11**, 90 (1961)

(2) (a) D F Peppard, G W Mason, J L Maier and W J Driscoll *J Inorg Nucl Chem* **4**, 334 (1957)
(b) D F Peppard, S W Moline and G W Mason *J Inorg Nucl Chem* **4**, 344 (1957)
(c) C F Baes, Jr, R A Zingaro and C F Coleman, *J Phys Chem* **62**, 129 (1958)
(d) D F Peppard, G W Mason and S McCarty, *J Inorg Nucl Chem* **13**, 138 (1960)
(e) D Dyrssen and F Krasovec, *Acta Chem Scand* **13**, 561 (1959)
(f) E Nakamura, *Bull Chem Soc Japan* **34**, 402 (1961)
(g) D Dyrssen and L D Hay, *Acta Chem Scand* **14**, 1100 (1960)
(h) G Duyckaerts, P Dreze and A Simon *J Inorg Nucl Chem* **13**, 332 (1960)
(i) K Kimura, *Bull Chem Soc Japan* **33**, 1038 (1960)
(j) K Kimura, *Bull Chem Soc Japan* **34**, 63 (1961)
(k) D F Peppard, G W Mason and S W Moline *J Inorg Nucl Chem* **5**, 141 (1957)

The extraction-inhibiting effects due to hydrolysis of the metal and to its co-ordination by the more commonly encountered complexing anions, are, in general, minimized by increasing the concentration of free hydrogen ion as is the tendency for tracer-level metallic species to adhere to surfaces Consequently, these acidic organo phosphorus esters seemed promising as efficient extractants for metallic radioactive nuclides contained in solutions prepared from environmental samples Following suitable treatment, the extract might then be used as the basis for the determination of nuclides

From the multiple viewpoints of universal availability of sample medium, reproducibility of data the presence of a number of inhibiting anions (whose effects must be overcome) including those of uric, hippuric, oxalic and sulphuric acids and of the acids of phosphorus, and the direct pertinence to the problem, human urine was chosen as the sample medium Accordingly, the extraction behaviour of tracer-level radioactive Ce(III), Pm(III), Y(III), Am(III), Cm(III), Pu(III), Th(IV), Np(IV), Pu(IV) and U(VI) in a system comprised of a solution of mono 2-ethyl hexyl phosphoric acid, H$_2$MEHP, in a variety of carrier diluents as the extractant phase and urine acidified with hydrochloric acid as the opposing phase was investigated

The variation of extraction and re-extraction conditions with the purpose of effecting the isolation of individual members of the foregoing series from an admixture was then investigated

(A study of the extraction of Th and U(VI) by di[para(1,1,3,3-tetramethylbutyl) phenyl] orthophosphoric acid, HDOϕP was included in order to demonstrate the inhibiting effect of complexing substances present in the urine)

Finally, the incorporation of extraction systems involving di 2-ethyl hexyl phosphoric acid, HDEHP, and tri n-octyl phosphine oxide, TOPO, into the overall flow-sheet for the purpose of final isolation of certain nuclides was investigated, and certain final volume reductions were accomplished through the use of "octyl pyrophosphate" as extractant (1a)

(3) (a) R R Grinstead, K G Shaw and R S Long, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy Geneva*, 1955 vol 8 p 71 United Nations (1956)
(b) C A Blake, Jr , C F Baes, Jr , K B Brown, C F Coleman and J C White, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy Geneva* 1958 vol 28 p 289 United Nations (1958)
(c) C A Blake, Jr , C F Baes, Jr and K B Brown, *Industr Engng Chem* **50,** 1763 (1958)
(d) D F Peppard, G W Mason, W J Driscoll and R J Sironen, *J Inorg Nucl Chem* **7,** 276 (1958)
(e) D F Peppard, G W. Mason, W J Driscoll and S McCarty, *J Inorg Nucl Chem* **12,** 141 (1959)
(f) D C Madigan, *J Appl Chem* **9,** 252 (1959)
(g) A S Chernyak and M L Navtanovich, *J Appl Chem* (*USSR*), Eng Trans **33,** No 1, 82 (1960) (Consultants Bureau Translation)
(h) V B Shevchenko and V S Smelov, *J Nucl Energy, Part A Reactor Science* **11,** 196 (1960)

(4) (a) D F Peppard, G W Mason and I Hucher, *J Inorg Nucl Chem* **18,** 245 (1961)
(b) D F Peppard, M N Namboodiri and G W Mason, *J Inorg Nucl Chem* **24,** 979 (1962)
(c) D F Peppard, G W Mason, I Hucher and F A J A Brandao, *J Inorg Nucl Chem* **24,** 1387 (1962)

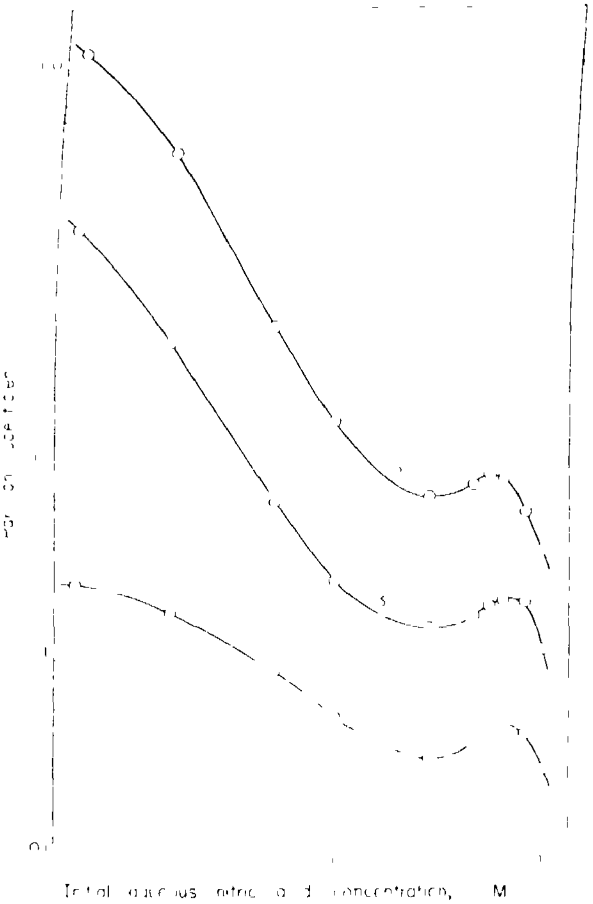


FIG. 1. Variation of partition coefficient with nitric acid concentration for the extraction of uranium (VI) by solutions of DEHPA in kerosene (figures on curves are DEHPA concentrations, M). $UO_2(NO_3)_2$ 5g/l 20°C.

If we assume that the initial decrease in partition coefficient shown in Fig. 1 is governed by an ion-exchange reaction similar to that in the extraction of uranium (VI) from sulphuric acid solution by DEHPA[6] viz.

$$UO_2^{2+}(a) + 2(HX)_2(o) \rightleftarrows UO_2X_4H_2(o) + 2H^+(a) \qquad (1)$$

where X represents the anion $(C_8H_{17}O)_2PO_2^-$, while (a) and (o) are indicative of aqueous and organic phases respectively then the following relationship would be obtained

$$\log 4E_c = \log K + 2\log (C_S - 4C_U)/C_H, \qquad (2)$$

where E_c is the partition coefficient, K the equilibrium constant, C_S the total DEHPA concentration C_U the organic phase uranium concentration and C_H the aqueous acidity. However, when values of $\log E_c$ were plotted vs. $\log (C_S - 4C_U)/C_H$ in

---

[6] C. A. BLAKE Jr., C. F. BAES, Jr., K. B. BROWN, C. F. COLEMAN and J. C. WHITE, *The Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva* 1958 Vol 28, p 289 United Nations (1958).

EXPERIMENTAL

Nomenclature

Mono 2-ethyl hexyl phosphoric acid and bis 2-ethyl hexyl phosphoric acid, respectively represented structurally as $(EHO)PO(OH)_2$ and $(EHO)_2PO(OH)$ where EH signifies the 2-ethyl hexyl group, are respectively represented symbolically as H_2MEHP and HDEHP In this usage,[2a-4d] the symbolic equivalents are H, a theoretically ionizable hydrogen atom, M, the prefix mono D, the prefix di (used interchangeably with bis), EH, the 2-ethyl hexyl group, and P, the phosphorus in an ortho phosphoric acid structure Similarly di[para(1,1,3,3-tetramethylbutyl)phenyl] phosphoric acid is symbolized HDOϕP, the "Oϕ" group signifying "octyl phenyl " (This compound is sometimes referred to as di para octyl phenyl phosphoric acid) The product purchased as octyl pyrophosphate is of unknown composition but probably contains both acidic and neutral esters of both ortho- and pyro-phosphoric acid Tri n-octyl phosphine oxide is represented as TOPO

The phosphorus ester is referred to as the extractant, and the solution of the ester in a carrier diluent is considered the extractant phase

The liquid in which the extractant is dissolved is termed the carrier diluent, without reference to participation in the extraction mechanism The diluents are definitely not to be considered inert

A component added to the extractant phase for the purpose of depressing the distribution ratio of a given nuclide is considered a negative synergist (1c)

The distribution ratio, *K*, for a specific nuclide is defined as the concentration of nuclide in the organic divided by the concentration of nuclide in the aqueous of the two equilibrated sensibly-immiscible phases, the concentrations being considered directly proportional to the radioactive-counting rates of samples prepared, under standard conditions, from suitable aliquots of the phases

Sources of materials

The H_2MEHP,(5) HDEHP(5) and HDOϕP(5) extractants were purified as described previously using mixtures obtained from Victor Chemical Co as the starting material Victor Chemical Co was also the source of octyl pyrophosphate, a viscous liquid

Tri n-octyl phosphine oxide, $(n\text{-}C_8H_{17})_3PO$, TOPO was obtained from Eastman Organic Chemical Department of Distillation Products Industries and treated as previously described(1c) before use

The 2-ethyl hexanol-1, used as a negative synergist was obtained from Union Carbide Chemical Co and the n-heptane from Phillips Petroleum Co The n-heptane was pre-conditioned before use in the Ce(IV) extraction, as described previously (2b)

The β-active tracer nuclides, 285 day ^{144}Ce, 2 6 year ^{147}Pm and 58 day ^{91}Y were obtained from the Isotopes Division of the Oak Ridge National Laboratory The α-active tracer nuclides 470 year ^{241}Am, 18 year ^{244}Cm 2 43 10^4 year ^{239}Pu, 2 2 10^6 year ^{237}Np 1 6 10^5 year ^{233}U (^{238}U ^{233}U mass ratio less than 0 03) and 8 0 10^4 year ^{230}Th (^{232}Th ^{230}Th mass ratio 0 1) were obtained from Argonne National Laboratory stocks Each of the foregoing tracers was further purified by means of liquid–liquid extraction techniques

Most of the urine samples were supplied by the same individual and, in general represented 24 hr composites

Preparation of samples

Each urine sample, upon receipt was acidified with 0 01 of its volume of 10 M HCl (In general a composite sample was acidified within 48 hr of the first collection)

Portions of these acidified samples of urine were then used both as "scrub" phases and as "feed" phases (following addition of radioactive nuclide)

Preparation of given valence state of nuclide

Both Ce(III) and U(VI) are stable species under the conditions employed so no especial precautions were taken

Neptunium was obtained as Np(IV) by treatment of stock Np tracer in aqueous HCl with hydro-quinone

Plutonium was utilized both as Pu(III) and Pu(IV)

The former, Pu(III), was obtained by reducing stock Pu tracer in 5 M HCl with 0 1 M hydroquinone followed by dilution to 0 5 M HCl and subsequent extraction of residual Pu(IV) into a 0 2

(5) D F PEPPARD, J R FERRARO and G W MASON, *J Inorg Nucl Chem* **7**, 231 (1958)

M solution of thenoyltrifluoroacetone (HTTA) in benzene diluent leaving Pu(III) in the aqueous phase.

The latter, Pu(IV), was prepared by extraction into 0.2 M HTTA (in benzene) from a 0.5 M HCl solution of stock Pu tracer containing NH_4NO_2 followed by re-extraction from the HTTA phase into 5 M HCl.

Determination of distribution ratios

The distribution ratio, *K*, of a specific nuclide was determined as reported in previous studies. In direct extraction the tracer radioactive nuclide was extracted from an aqueous into an organic phase. In reverse extraction the nuclide was re-extracted from an organic into an aqueous phase. For assay known aliquots of the centrifuged phases were evaporated, by induction heating, on 3 mil platinum disks $\frac{15}{16}$ in. in diameter. These samples were then subjected to alpha and/or beta counting using suitable aluminum absorbers as needed.

The Am and Cm data are essentially identical. Therefore, only Am data are reported in detail.

All data were obtained at 22 ± 2°C.

Testing of flow sheets

Measured quantities of assayed solutions of the specific nuclides in approximately 10 M HCl were added to a 500 ml sample of urine after acidification with 5.0 ml of 10 M HCl. (The total volume of tracer solution added was less than 0.3 ml.) The total sample then contained approximately 2×10^5 disintegration/min of each tracer employed. (It should be noted that in the presentation of data no attempt to convert counts/min to disintegrations/min, since within experimental error the conversion factor under given counting conditions is the same for the sample prepared from the equilibrated organic phase as for one prepared from the corresponding equilibrated aqueous phase.)

Standard separatory funnels and stoppered cylinders were used. Except where separatory funnels were employed, transfers were made by means of transfer pipettes. (These were fabricated from 12 mm o.d. glass tubing drawn down to approximately 1.5 mm o.d. at the lower 5 in. and to approximately 5 mm o.d. at the top. The bulb is filled by suction applied by a hypodermic syringe attached to the top of the pipette through a short length of rubber tubing.) These pipettes were considered expendable, and were not reused for fear of introducing contamination at a later step.

Contact periods of 3 min were employed.

Final individual products were identified, and respective radiochemical purities proved to be in excess of 95 per cent, by a combination of α-pulse analyses, determination of β-absorption curves and application of further separations techniques. For example, an alpha pulse analysis of the Pm–Am product showed the presence of less than 5 per cent extraneous α-activity in the activity associated with ^{241}Am.

RESULTS AND CONCLUSIONS

Comparative extraction data for Th(IV) and U(VI) from acidified urine into 0.1 F solutions of HDOφP and of H_2MEHP, in carbon tetrachloride diluent, are presented in Table 1. An extremely large inhibiting effect at lower acidities is demonstrated by the HDOφP Th data. From the data reported for the HDOφP (toluene) vs. HCl system(2a, 1b) and from data presently obtained for the HDOφP (CCl_4) vs. HCl system it may be concluded that the *K* values for Th from 1.0 M H^+ and from 0.1 M H^+ should be greater than 10^6 and greater than 10^{10} respectively. These figures are to be compared with the observed respective values of 1.0×10^3 and 12.

Further, in the absence of an acid-sensitive inhibiting effect, the *K* for Th should vary inversely approximately with the fourth-power of the H^+ concentration. Instead, it increases with increasing H^+ concentration. It is, therefore, concluded that the inhibiting effect, presumably due to complexing of Th^{4+} in the aqueous phase, is highly acid-sensitive, increasing rapidly with decreasing acidity.

The inhibition of the extraction of U(VI) in the same system is far less marked. The *K* values for U(VI) into 0.1 F HDOφP (CCl_4) from 1.0 M and from 0.10 M HCl respectively, no other solutes present, are approximately(6) 2×10^2 and 5×10^4.

The *K* values for Th into 0 1 F H_2MEHP (CCl_4) from 1·0 M HCl and from 0 10 M HCl, no other solutes present, are too high to be measured, but from an extension[(6)] of reported[(1a,1c)] studies, lower limits may be set It is concluded that the respective values are greater than 10^7 and greater than 10^9 A large inhibiting effect is operative in this system also However, the *K* values for Th increase with decreasing H concentration

Again, the inhibition of the extraction of U(VI) in the same system is relatively minor, the *K* from 1 0 M H^+ (Table 1) being almost identical with that from 1 0 M HCl, no other solutes present [(1c 6)]

TABLE 1 --DISTRIBUTION RATIOS OF Th(IV) AND U(VI) INTO 0 10 F HDOϕP AND 0 10 F H_2MEHP (CARBON TETRACHLORIDE DILUENT) FROM ACIDIFIED URINE, V_O/V_A 1 0

H^+* (M)	*K*† 0 10 F HDOϕP Th		U(VI)		0 10 F H_2MEHP Th		U(VI)	
0 10	12		1 2	10^3	1 8	10^4	3 7	10^3
0 20	56		5 9	10^2	1 6	10^4	2 2	10^3
0 50	5 4	10^2	1 6	10^2	1 1	10^3	1 5	10^3
0 75	4 9	10^2	1 2	10^2	9 6	10^2	9 5	10^2
1 0	1 0	10^3	88		4 1	10^2	4 6	10^2

* Hypothetical acidity calculated on the basis of added HCl, disregarding buffering action of other components of the solution

† All *K* values of Table 1 obtained with aliquots of a single composite urine sample, not the sample of Tables 2 and 3 but supplied by the same individual

From the data of Table 1, it was concluded that a 0 10 F H_2MEHP (CCl_4) vs acidified urine ("0 1 M H^+") system could be employed in effecting the transfer of Th(IV) and U(VI) from a urine sample to an organic phase

The extraction behaviour of selected lanthanides (III) and actinides (III) as a function of H^+ concentration was then investigated Chlorobenzene was employed as a diluent in this study, but since, the *K* for actinides (III) and lanthanides (III) in H_2MEHP vs HCl systems is relatively insensitive to the diluent employed, if the diluent is neither a hydrogen bond donor nor acceptor,[(6)] the data may be considered comparable to those in a system employing carbon tetrachloride as diluent In Table 2 these data are presented along with those for Th Pu(IV) Np(IV)?, Pa and U(VI)

It may be noted that the Th and U(VI) data are closely comparable to those of Table 1 From Table 2, it is evident that M(III) M(IV) and M(VI) may all be extracted with acceptably high *K* values from 0 1 M H with the exception of Np(IV) (The data for Pa, presumed to be present as Pa(V), are included for comparison) From published data[(1a)] and extended study[(7)] of the extraction of Np(IV) by H_2MEHP from HCl the *K* values for Np(IV), in the absence of inhibitory effects would be expected to exceed 10^5 at each of the H^+ concentrations employed The extraction of U(IV) has been investigated only at H^+ concentrations greater than 6 M, the *K* being greater than 1 10^4 From these data, it is evident that U may be extracted as U(IV) or U(VI)

---

(6) D F PEPPARD, G W MASON and S McCARTY Unpublished data

(7) D F PEPPARD, G W MASON, R J RARIDON and S McCARTY Unpublished data

Table 2 —Distribution ratios for various elements into 0 10 F H_2MEHP (chlorobenzene diluent) from acidified urine V_O/V_A = 1 0

H⁺* (M)	K†									
	Ce(III)	Pm	Y	Am(III)	Th	Pu(III)	Pu(IV)	Np(IV)?	Pa	U(VI)
0 10	3 0 10^2	6 7 10^2	7 6 10^2	4 7 10^2	3 4 10^4	5 9 10^2	1 2 10^3	9 0	92	4 2 10^3
0 20	72	1 2 × 10^2	1 4 10^2	70	1 3 10^4	1 1 10^2	5 7 10^2	1 1	20	2 4 10^3
0 50	6 6	8 2	12	5 2	6 2 10^3	11	2 1 10^2	11	1 0 10-	1 9 10^3
0 75	2 2	2 4	3 8	1 5	1 2 10^3	3 7	3 4 10^2	77	5 7 10^2	7 6 10^2
1 0	1 4	2 0	2 5	1 3	1 0 10^3	2 0	1 4 × 10^2	43	7 5 10^2	5 4 10^2

* Hypothetical acidity calculated on the basis of added HCl, disregarding buffering action of other components of the solution

† All K values of Tables 2 and 3 obtained with aliquots of a single composite urine sample Each nuclide separately present, except for ^{147}Pm and ^{241}Am which were simultaneously present The valence indicated is that of the nuclide as added to the acidified urine samples

Table 3 —Distribution ratios for various elements into 0 02 F H_2MEHP (composite diluent CCl_4 toluene, 40 60 vol/vol) from acidified urine, V_O/V_A = 0 10

H⁺* (M)	K†							
	Ce(III)	Pm	Y	Am(III)	Th	Pu(III)	Pu(IV)	U(VI)
0 10	4 1 × 10^2	4 4 × 10^2	4 3 10^2	3 0 10^2	6 2 10^4	6 2 10^2	4 3 10^3	7 9 × 10^2
0 50	5 5	8 0	8 6	5 6	1 5 × 10^3	12	4 6 × 10^2	2 9 × 10^3

* Hypothetical acidity calculated on the basis of added HCl, disregarding buffering action of other components of the solution

† All K values of Tables 2 and 3 obtained with aliquots of a single composite urine sample Each nuclide separately present, except for ^{147}Pm and ^{241}Am which were simultaneously present The valence indicated is that of the nuclide as added to the acidified urine samples

and that Pu may be extracted as Pu(III) or Pu(IV). Presumably Pu(VI) may also be extracted with a high K. However, the presence of Pu in this oxidation state in urine acidified with HCl seems most unlikely.

From Table 2, it is evident that Ce, Pm, Y, Am, Th, Pu and U may be extracted with K values ranging from 3×10^2 to 3×10^4 from acidified urine (0.1 M H^+) without regard to valence control of any element. It should be noted that in both Tables 1 and 2 the volume ratio, V_0/V_A, is 1.0. It was found that in the systems of Table 2, if the volume ratio, V_0/V_A, was 0.1, the K values were markedly decreased. Since the K was found to be independent of the concentration of nuclide studied, it was assumed that this decrease was due to the extraction of extraneous solutes present in the urine, the net result being that the concentration of "free" H_2MEHP available was materially reduced. In order to partially compensate for this effect, the initial concentration of H_2MEHP was doubled. Further, the chlorobenzene diluent was replaced by a composite diluent consisting of a 40 60 vol/vol mixture of CCl_4 and toluene. The resulting extractant solution (becoming the lower phase) disengages from equilibrated acidified urine more readily than does the solution of Table 2, and by the addition of a relatively small quantity of n-heptane and/or 2-ethylhexanol-1 may be converted to a phase lighter than dilute aqueous mineral acid. (The value of these properties will become evident in devising a flow sheet.)

From the data of Table 3, it is apparent that Ce, Pm, Y, Am, Th, Pu and U may all be extracted into 0.2 F H_2MEHP (composite diluent CCl_4 toluene 40 60 vol/vol from acidified urine (0.1 M H^+) with K values of 3×10^2 or greater, under conditions employing a volume ratio of 0.1. In other words, from a 1,000 ml portion of acidified urine, the least extractable of these would report in approximately 97 per cent yield to a 100 ml portion of equilibrated extractant phase.

For purposes of volume reduction of sample, it is desirable to extract the indicated radioactive nuclides into a volume of extractant phase as small, relative to the volume of the initial urine, as is consistent with acceptable yield of nuclides. Consequently, it was decided to use two 0.1 volume portions of extractant in the initial extraction step. (From the data of Table 3, the least extractable nuclide should report in 99.9 per cent yield to the combined extracts.)

In making two successive 0.1 volume extractions, it is convenient to use a system in which the extract is the more dense phase so that following phase disengagement it may be separated readily without transfer of the bulk urine. Analogously, in returning the nuclides to an aqueous phase, and at the same time realizing a volume reduction, it is advantageous to employ a system in which the aqueous phase is the more dense.

In experiments represented by the data of Table 4, the purpose of the n-heptane is to reduce the density of the extractant phase, and the 2-ethyl hexanol-1 serves both to reduce the density and to negatively synergize(1c) the extraction of the pertinent nuclides by partially inactivating the H_2MEHP extractant. From reported studies(1c) it is evident that an "intermediate negative synergistic effect" which will permit return of M(III) cations to an aqueous phase but retention of M(IV) and M(VI) cations in the organic phase may be realized. Such a system is represented in Table 4. In this system, the 0.1 M NH_4NO_2 ensures the absence of Pu(III), the oxidation of Pu(III) to Pu(IV) being very rapid.

The organic phases of Table 5 may be considered as obtained by addition of 10 volumes of 2-ethyl hexanol-1 to 20 volumes of the organic phase of Table 4. An

TABLE 4.—DISTRIBUTION RATIOS FOR VARIOUS ELEMENTS IN THE SYSTEM 0.10 F H_2MEHP (COMPOSITE DILUENT CCl_4, TOLUENE, n-HEPTANE AND 2-ETHYL HEXYL ALCOHOL IN RELATIVE VOLUMES 4, 6, 5, 5) VS AQUEOUS 0.20 M HCl (WHICH IS 0.01 M IN NH_4NO_2) $V_O/V_A = 1.0$

Element	Ce(III)	Pm	Y	Am(III)	Th	Pu†	Pu(IV)	U(VI)
*K**	4.4×10^{-3}	3.2×10^{-3}	2.2×10^{-2}	2.2×10^{-3}	9.8×10^{3}	2.9×10^{3}	3.4×10^{3}	35

* Each nuclide separately present except for ^{147}Pm and ^{241}Am which were simultaneously present. Each *K* value determined by scrubbing an organic extract with a barren aqueous phase. Each organic extract prepared by extracting the nuclide from an aliquot of a single composite urine sample into E-1, then diluting with an equal volume of D-1.

† Added as Pu(III) to the urine sample. Oxidized to Pu(IV) by the nitrite in the scrub.

extract, following suitable treatment as in Table 4, will contain only Th, Pu and U as shown in Table 5. (Np is included for comparative purposes, since the behavior of Np(IV) is quite reproducible and the K values are of acceptable magnitude at every step except in the original extraction, Table 2.) The aqueous phase employed is H_2SO_4 rather than HCl, since much lower K values at a given H^+ concentration are thereby attained.

It is evident from Tables 4 and 5 that through selective anti-synergistic action two aqueous products, P-3 and P-2 containing respectively Ce, Pm, Y, Am and Cm and Th, Pu, U and Np(?), may be obtained. (It is noted in the Experimental section under "Determination of distribution ratios" that the Am and Cm data are nearly identical in each of the systems investigated in this study.) These two aqueous phases are the final products of Flow Sheet-1 which is based upon Tables 3, 4 and 5.

TABLE 5. DISTRIBUTION RATIOS FOR VARIOUS ELEMENTS IN THE SYSTEM 0.067 F H_2MEHP (COMPOSITE DILUENT CCl_4, TOLUENE, n-HEPTANE AND 2-ETHYL HEXYL ALCOHOL IN RELATIVE VOLUMES 4, 6, 5 AND 15) vs AQUEOUS 0.5 M AND 1.0 M H_2SO_4. $V_O/V_A = 1.0$

H_2SO_4 (M)	K*			
	Th	Pu(IV)	Np(IV)	U(VI)
0.5	8.4×10^{-2}	9.1×10^{-2}	4.1×10^{-2}	3.8×10^{-2}
1.0	9.7×10^{-3}	8.6×10^{-3}	6.4×10^{-3}	9.3×10^{-3}

* Each nuclide separately present. A pregnant extract of desired nuclide prepared by extraction into a 0.2 F H_2MEHP (diluent CCl_4 toluene, 40:60 vol/vol) phase from an aliquot of a common acidified urine solution. Unit volume of this extract then diluted with unit volume of D-1 and unit volume of D-2. The resulting organic phase then contacted with an equal volume of aqueous 0.5 or 1.0 M H_2SO_4. The valence indicated is that of the nuclide as added to the acidified urine sample.

Tables 6, 7 and 8 pertain to the mutual separation of Th, Pu and U from the mixture, P-2, obtained as a product of Flow Sheet-1 and constitute the basis of Flow Sheet-2. The mixture obtained from Flow Sheet-1 consists of Th, Pu and U in 1.0 M H_2SO_4. As a preliminary step in effecting their mutual separation, these elements are returned to an organic phase, with an accompanying volume reduction. The K values are given in Table 6. (The magnitude of the "depressing" effect of 2-ethyl hexanol-1 is evident upon comparison of Tables 5 and 6.)

From this organic extract, Pu is returned to an aqueous phase as Pu(III) following reduction by hydroquinone, accompanied by U(VI) under conditions permitting retention of Th and Np(IV) in the organic extract. The pertinent data are given in Table 7.

The mutual separation of U and Pu is then accomplished by extraction of U(VI) into a toluene solution of TOPO from 6 M HCl, Pu(III) remaining preferentially in the aqueous phase as indicated by the data of Table 8.

Tables 9 and 10 pertain to the further partitioning of the Ce, Pm, Y and Am product, P-3, of Flow Sheet-1 and constitute the basis of Flow Sheet-3. From Table 9, it is evident that a 0.30 F HDEHP (toluene) vs 0.2 M HNO_3 system serves to separate Y from Ce(III), Pm and Am, the Y reporting to the organic phase. Further the Y may be returned to an aqueous phase 4.0 M in HCl.

TABLE 6 DISTRIBUTION RATIOS FOR VARIOUS ELEMENTS IN THE SYSTEM 0 20 F H_2MEHP (COMPOSITE DILUENT CCl_4 TOLUENE, 40 60 VOL/VOL) VS FRESHLY PREPARED 0 5 M AND 1 0 M H_2SO_4 RE-EXTRACTS OF TABLE 5 V_0/V_A = 1 0

H_2SO_4 (M)	K			
	Th	Pu(IV)	Np(IV)	U(VI)
0 5	3 3 10^3	4 5 10^2	1 8 10^2	6 0 10^2
1 0	1 5 10^3	1 6 10^2	1 1 10^2	2 0 10^2

TABLE 7—DISTRIBUTION RATIOS FOR Th, Np(IV), U(VI) AND Pu(III) IN THE SYSTEM 0 2 F H_2MEHP (COMPOSITE DILUENT CCl_4 TOLUENE 40 60 VOL/VOL) VS AQUEOUS 12 M HCl*

Element	Th	Np(IV)	U(VI)	Pu(III)
K	8 10^4	7 10^2	9 10^{2}	8 × 10^{2}

* The symbol indicates "greater than

TABLE 8 DISTRIBUTION RATIOS FOR U(VI) AND Pu(III) IN THE SYSTEM 0 20 F TOPO (TOLUENE DILUENT) VS AQUEOUS HCl

HCl (M)	K	
	U(VI)	Pu(III)
6 0	6 7 × 10^2	1 2 10^{2}
12 0	35	3 5 10^{-1}

TABLE 9 DISTRIBUTION RATIOS FOR VARIOUS M(III) IN THE SYSTEM 0 30 F HDEHP (TOLUENE DILUENT) VS AQUEOUS 0 20 M HNO_3* AND 4 0 M HCl

M(III)	Ce(III)	Pm	Y	Am
K, 0 2 M HNO_3	4 1 10^{3}	4 2 × 10^{2}	26 2	1 1 × 10^{-2}
K, 4 0 M HCl	1 10^{4}	1 × 10^{4}	~2 10^{-3}	< 1 × 10^{4}

* These data are consistent with those of References (2a) and (3d) in which other mineral acids were employed and with those of Reference (8) in which 0 20 M HNO_3 was used The symbol indicates "less than "

TABLE 10—DISTRIBUTION RATIOS FOR Ce(IV) AND VARIOUS M(III) IN THE SYSTEM 0 30 F HDEHP (*n*-HEPTANE DILUENT) VS 8 0 M HNO_3*

Element	Ce(IV)	Ce(III)	Pm(III)	Am(III)
K	5 × 10^3	~2 × 10^{-3}	2 × 10^{3}	< 2 × 10^{3}

* These data are consistent with those of References (2b) and (2k) The symbol indicates "less than "

---

(8) M A MANDIL, G W MASON and D F PEPPARD, *Industr Engng Chem Process Design and Engineering Quarterly* 2, 106 (1963)

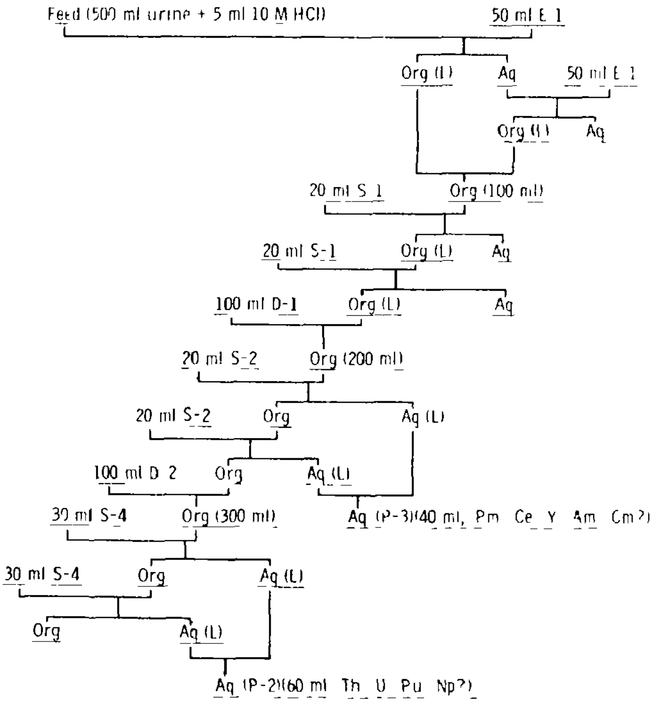


Fig. 1—Flow Sheet-1 Products P-2 and P-3 of Flow Sheet-1 are the respective feeds to Flow Sheets 2 and 3 (L) signifies lower phase

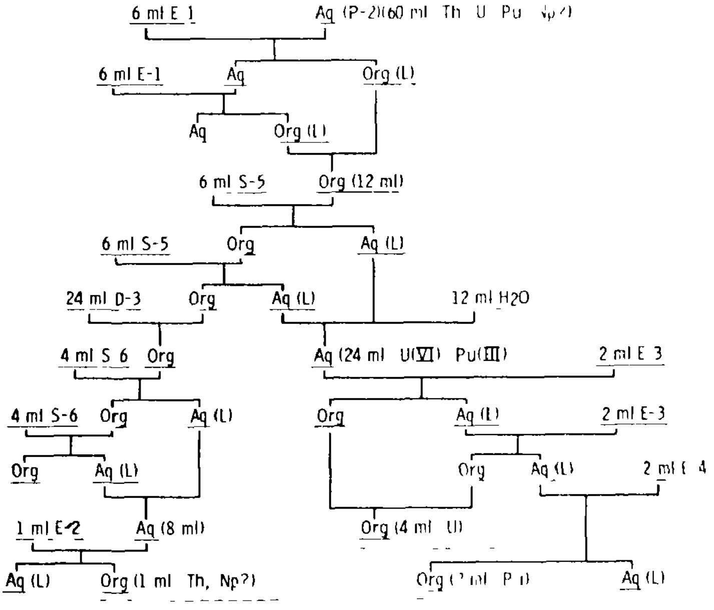


Fig. 2—Flow Sheet-2 Separation into (Th Np?) U and Pu products (L) signifies lower phase

The Ce, Pm, Am mixture may now be partitioned further by taking advantage of the tetravalent state of Ce The system of Table 10, and that reported for the extraction of Bk(IV)$^{(2h)}$ and Ce(IV) $^{(2k)}$ serves to separate Ce(IV) from Pm(III), Am(III) and Cm(III) with a separation factor, β defined as $K_{Ce(IV)}/K_{M(III)}$, greater than 10^6 From an analytical view, the separation of this group of elements is complete at this point, in the absence of Cm(III), since Pm and Am may each be determined in the presence of the other by combined alpha counting for Am and β-counting, in the presence of absorber to screen out the alpha activity due to Am, for Pm

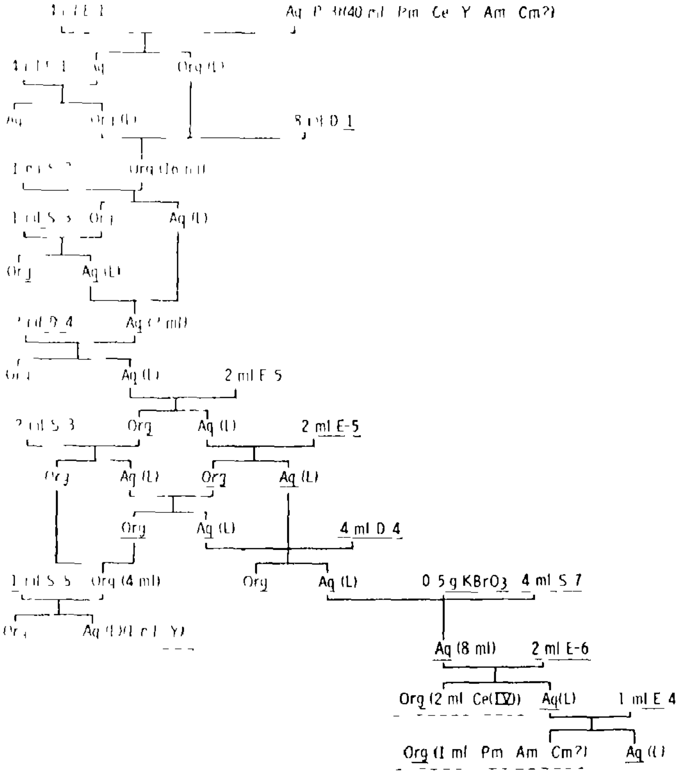


FIG 3 – Flow Sheet-3 Separation into Y, Ce, and (Pm, Am, Cm ?) products (L) signifies lower phase

On the basis of the foregoing data, Flow Sheets 1, 2 and 3 were devised keeping in mind the requirements of nearly quantitative extraction of each of the radioactive elements from the initial sample of urine, nearly complete removal of contaminant radioactive elements from a product element which in turn must be obtained in nearly quantitative yield, a volume reduction at every stage possible, ease of operation by means of making the organic phase either the upper or lower phase and by avoiding the necessity for intermediate evaporations, and a final product in a small volume so that a suitably large portion of it might be evaporated on a platinum disk for radiometric assay

In order to confine the presentation of Flow Sheets to a reasonable size, it was necessary to introduce symbols to represent phases of specific composition The

0.5 and 1.0 M acid it was found that Equation (2) is not satisfied. Furthermore, as values of the partition coefficient for 0.1 M DEHPA in kerosene are greater than ten, it is likely that extraction under these conditions involves formation of a polymeric uranium–DEHPA complex[7] as in sulphuric acid solutions at low acidity:[1]

$$UO_2X_4H_2(o) + UO_2^{2+}(a) + (HX)_2(o) \rightleftarrows (UO_2)_2X_6H_2(o) + 2H^+(a) \qquad (3)$$

i.e. an overall reaction

$$2UO_2^{2+}(a) + 3(HX)_2(o) \rightleftarrows (UO_2)_2X_6H_2(o) + 4H^+(a) \qquad (4)$$

This leads to the following relationship

$$\log 4E_U^{o} = \log K_1 + 2 \log (C_X - 2C_U)/C_H \qquad (5)$$

where K_1 is a constant. When values of $\log E_U$ were plotted vs. $\log (C_X - 2C_U)/C_H$ in 0.5 and 1.0 M acid it was found that Equation (5) is satisfied, the slopes of the lines being 1.9 and 1.8 in 0.5 M and 1.0 M HNO_3 respectively. Thus it appears that at low nitric acid concentrations uranium is extracted in accordance with Equation (4).

If we assume that at higher acidities n molecules of the DEHPA dimer combine with each uranium (VI) ion by a reaction similar to that observed with TBP, viz.

$$UO_2^{2+}(a) + 2NO_3^-(a) + n(HX)_2(o) \rightleftarrows UO_2(NO_3)_2(HX)_{2n}(o) \qquad (6)$$

then the following relationship would be expected

$$\log 2^n E_U = \log K_2 + n \log (C_X - 2nC_U) \qquad (7)$$

where K_2 is a constant. When the values of E_U were plotted vs. $\log (C_X - 2nC_U)$ for values of $n = 1$ and 2 in 6 M HNO_3 the slopes of the lines were 1.6 and 1.3 for $n = 1$ and 2 respectively. However, since either or both of reactions (1) and (3) will also occur to some extent at higher acidities the observed values of the partition coefficient are probably higher than if extraction showed a nitrate ion dependency due to Equation (6) alone. As the slope of the line using $n = 1$ may therefore be greater than unity, we assume that $n = 1$ in Equation (6), i.e.

$$UO_2^{2+}(a) + 2NO_3^-(a) + (HX)_2(o) \rightleftarrows UO_2(NO_3)_2(HX)_2(o) \qquad (8)$$

(b) *Dependence on uranium concentration*

When uranyl nitrate solutions containing 1.0 and 6.0 M nitric acid are extracted into 0.1 M DEHPA in kerosene at 20 °C the organic phase uranium concentration was found to increase with increasing initial aqueous uranium concentration towards a limiting value (0.05 M), indicating that two molecules of DEHPA combine with each uranium ion under these conditions.

(c) *Dependence on organic phase activity*

The extraction of acid from uranyl nitrate solutions (5 g/l) into 0.1 M DEHPA in kerosene was included at 20 °C with the results shown in Fig. 2, which also gives data for the extraction of acid in the absence of uranium.

In the absence of uranium the acidity of the organic phase is approximately constant below 3 M and increases with increasing aqueous acidity above this concentration. In the presence of uranium the organic phase acidity is less than in its absence

---

[7] C. F. Baes Jr., R. A. Zingaro and C. F. Coleman, *J. Phys. Chem.* **62**, 129 (1958).

TABLE 11.—LIQUIDS EMPLOYED IN FLOW SHEETS 1, 2 AND 3

Symbol*	Composition	Density†
E-1	0.20 F $\mathrm{H_2MEHP}$ ($\mathrm{CCl_4}$ + toluene, 40:60 vol/vol)	1.14
E-2	0.20 F $\mathrm{H_2MEHP}$ (toluene)	0.873
E-3	0.20 F TOPO (toluene)	0.868
E-4	"2% octyl pyrophosphate" (toluene)	0.871
E-5	0.30 F HDEHP (toluene)	0.873
E-6	0.30 F HDEHP (n-heptane)	0.709
D-1	n-heptane + 2-ethyl hexanol-1 50:50 vol/vol	0.753
D-2	2-ethyl hexanol-1	0.834
D-3	n-heptane + 2-ethyl hexanol-1, 25:75 vol/vol	0.802
D-4	n-heptane	0.682
S-1	0.1 M HCl	1.00
S-2	0.1 M HCl, 0.01 M $\mathrm{NH_4NO_2}$ (freshly prepared)	1.00
S-3	0.2 M $\mathrm{HNO_3}$	1.00
S-4	1.0 M $\mathrm{H_2SO_4}$	1.06
S-5	12 M HCl, 0.1 M hydroquinone (freshly prepared)	1.18
S-6	6 M HCl	1.10
S-7	16 M $\mathrm{HNO_3}$	1.42
S-8	4 M HCl	1.07
	(E-1) + (D-1), 1:1 by vol	0.945
	(E-1) + (D-1) + (D-2), 1:1:1 by vol	0.909
	(E-1) + (D-3) 1:2 by vol	0.910

* The letters E, D and S, respectively, signify extractant, diluent and scrub.

† Values obtained by weighing a 10 ml portion at 22 ± 1°C.

significance of these symbols is shown in Table 11. The reasons for using these various solutions will be made clear by reference to the data of Tables 3–10.

Choice of the specific volume ratios employed and the number of extractions and/or scrubs was based upon considerations of completeness of extraction of a given element and upon decontamination of one element with respect to another considered as a contaminant.

Steps involving the use of octyl pyrophosphate as extractant were introduced for the purpose of effecting final volume reductions. This extractant is utilized because of its effectiveness in removing M(III), M(IV) and M(VI) ions from an aqueous phase.

The extractants E-5 and E-6, respectively 0.3 F HDEHP (toluene) and 0.3 F HDEHP (n-heptane), are not interchangeable. Toluene can not be used as the diluent in extracting tracer-level Ce(IV) because of its inherent reducing action; and if n-heptane is used as the diluent in the Y-separation step, the K values for Pm and Am are too high.

From the data of Table 12 it may be concluded tentatively that any one of the pertinent nuclides present in human urine, as voided, may be isolated in high purity in a yield of 50 per cent or greater. Such a conclusion, however, is based upon a questionable assumption and must be considered with due caution, since it has not been demonstrated that a given nuclide present in a urine sample as voided will be extracted with the same K value as that characteristic of the nuclide added as a spike. On the other hand, in the analysis of a given sample probably only a relatively small portion of the composite flow sheets, Flow Sheets 1, 2 and 3, need be employed, and consequently the yields would be increased.

DISCUSSION

For ease of operation it is sometimes desirable to render the extract (in the present context, the organic phase) the upper or the lower of the two mutually equilibrated phases at will. Fortunately, the extractant, H_2MEHP, extracts each of the pertinent M(III), M(IV) and M(VI) species with a K nearly independent of the diluent employed if the diluent choice is restricted to aromatic and aliphatic hydrocarbons and their chlorinated variants. (These K values are affected drastically by certain oxygen-containing diluents.)(1c) Consequently, a hydrocarbon or a halogenated hydrocarbon of a suitable density may be chosen as diluent for the H_2MEHP extractant to render the organic phase either more dense or less dense than the opposing aqueous phase.

TABLE 12.—ISOLATION OF PURIFIED NUCLIDES FROM SPIKED URINE SAMPLES* BY APPLICATION OF FLOW SHEETS 1, 2 AND 3

Nuclide	Type emitter	Recovery (final product) (%)	
		Run 1	Run 2
Ce^{144}	β	54	50
Pm^{147}	β	54	48
Y^{91}	β	46	42
Am^{241}	α	52	48
Th^{230}	α	51	47
U^{233}	α	91	96
Pu^{239}	α	76	82

* Each sample consisted of a 500 ml portion of urine acidified with 5 ml of 10 M HCl and containing accurately known quantities of the pertinent nuclides, approximately 2×10^5 disintegration/min of each.

Thus, in the first part of Flow Sheet-1, a 505 ml portion of aqueous feed is contacted successively with two 50 ml portions of extractant having a density greater than that of the feed. Consequently, the two extracts are drained from the bottom of a separatory funnel without necessitating transfer of the urine sample. (Densities, pertinent to each of the steps in the three Flow Sheets are presented in Table 11.)

In those instances in which the pertinent elements differ in valence, their mutual separation is accomplished, in part, by use of selective re-extraction into aqueous HCl as previously reported for M(III), M(IV) and M(VI).(1a) The data of Table 4 indicate the ready separation of Th(IV), Pu(IV) and U(VI) as a group from Ce(III), Pm, Y and Am(III) and those of Table 7, that of Th, and Np(IV), from U(IV) and Pu(III). The mutual separation of U(VI) and Pu(III) may also be accomplished by use of a more dilute HCl solution vs. an H_2MEHP (diluent)(1a) system, but the system represented in Table 8 is more readily applied.

The high K values for the M(III), M(IV) and M(VI) elements of interest from acidified urine (and from dilute HCl) into a solution of H_2MEHP in a diluent which is not negatively synergistic, Tables 2 and 3, are desirable from the viewpoint of preparing a concentrated extract of the pertinent elements in good yield. However, returning these elements to an aqueous phase presents a new problem. The M(III) elements may be re-extracted into a moderately concentrated HCl phase, the *K* values being nearly inversely third power dependent upon the H^+ concentration in the aqueous phase The return of U(VI) to an aqueous 12 M HCl phase may also be accomplished However, M(IV) can not be returned to an aqueous phase by increasing the concentration of mineral acid Dilution of the extract by more of the initial diluent is of no help, since the *K*, in each case, is approximately first-power dependent upon the concentration of H_2MEHP Consequently, each of these elements is returned to an aqueous phase by the controlled addition of a negatively synergistic agent, 2-ethyl hexyl alcohol, to the extract See Tables 4 and 5 Under the conditions specified in Table 4, the *K* for M(IV) is greater than 10^3, that for U(VI) 35 and those for M(III) less than 0 025 The addition of more negative synergist, Table 5, serves to lower the *K* for M(IV) sufficiently to permit return to an aqueous phase (The aqueous phase employed here is H_2SO_4 rather than HCl in order to lower the *K* for U(VI) as much as possible)

Due to the extremely high *K* values for the elements examined in the absence of a negative synergist and the correspondingly low *K* values in the presence of a negative synergist, it is possible to achieve very useful volume reductions in a few steps For example, at the conclusion of Flow Sheet-1 two intermediate "product" phases, P-2 (Th, U, Pu, Np?) and P-3 (Pm, Ce, Y, Am, Cm?), of respective volumes 60 ml and 40 ml, result from the processing of a 500 ml sample of urine In some instances, for example if Pm and Am are the only radioelements which may be present, the analysis is complete at this point

The separation of Y from Ce, Pm and Am is dependent upon the pronounced difference in *K* values in the HDEHP (toluene) vs aqueous mineral acid systems, Table 9, Y being preferentially extracted Since the *K* values are inversely third power hydrogen ion dependent, Y may be returned to a 4 M HCl phase The separation of Ce from Pm and Am is based upon the preferential extraction of Ce(IV) (2b) Table 10, in the HDEHP (n-heptane) vs 8 0 M HNO_3 system

Since this method of analysis requires no evaporation of the urine (and perhaps subsequent ashing) the possibility of loss of radionuclides by adsorption on the surfaces of equipment is minimized Each of the indicated steps is simple and may be performed rapidly, and no special equipment, other than that normally used in radiochemistry, is required (The contacting equipment, at critical steps, may be considered "throw-away ")

Occasionally, phase disengagement in the first step of Flow Sheet-1 is poor In such an instance, the extract (lower phase) contains some of the aqueous phase which must be removed by centrifugation However this is not difficult, since the volume is small

Although this study was restricted to urine samples it is evident that this system of analysis, with minor modifications, is applicable to a wide variety of environmental and biological samples including soil, vegetation, egg shells bones milk grain etc Application to the "indirect" determination of ^{90}Sr through direct analysis for ^{90}Y is especially promising

For certain elements, such as Sr and Ba, HDOϕP shows considerable promise,(9) although from Table 1 it is evident that Th may be extracted only from a highly acidic urine

---

(9) D F Pippard, G W Mason, S McCarty and F D Johnson, *J Inorg Nucl Chem* **24**, 321 (1962)

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 1191 to 1199. Pergamon Press Ltd. Printed in Northern Ireland

NOTES

Exchange properties of ammonium salts of 12-heteropolyacids—V. Sorption of alkali metals on ammonium phosphomolybdatotungstate

(*Received* 17 *December* 1962, *in revised form* 3 *March* 1963)

HETEROPOLYACIDS have been used for the precipitation of heavy alkali metals[(1, 2)] and their exchange properties have been described.[(3, 4)] Ammonium phosphomolybdate[(4)] and ammonium phosphotungstate[(5)] have been thoroughly investigated, and the present study describes the exchange properties of ammonium salts of phosphomolybdatotungstic acid (NH_4PMoW) with various molar ratios of Mo:W.

The uptake was studied under both static and dynamic conditions[(6)] using acid ammonium salts of phosphomolybdatotungstic acids with varying molar ratios of Mo:W (4:8, 6:6, 8:4). These were precipitated with an excess of 1 M NH_4NO_3 from aqueous solutions of the free heteropolyacids obtained by the etherate method;[(7)] analyses corresponded to the formula in Table 1.

TABLE 1

Ion exchanger	Formula	Mol. Wt.
$NH_4PMo_4W_8$	$(NH_4)_{2.55}H_{0.45}[PMo_4W_8O_{40}]$ 6,5 H_2O	2666
$NH_4PMo_6W_6$	$(NH_4)_{2.58}H_{0.42}[PMo_6W_6O_{40}]$ 7,6 H_2O	2510
$NH_4PMo_8W_4$	$(NH_4)_{2.48}H_{0.52}[PMo_8W_4O_{40}]$ 5,7 H_2O	2299

Figure 1 shows the uptake of Cs and Rb as a function of NH_4^+ ion concentration and demonstrates the ion-exchange nature of the process. Caesium is sorbed more easily than rubidium, in agreement with the values of the crystallographic radii.[(8)] K_d(Cs) decreases in the order $NH_4PMo_8W_4$ > $NH_4PMo_6W_6$ > $NH_4PMo_4W_8$ and from the measured K_d values for caesium and rubidium the theoretical value of the separation factor α_{Rb}^{Cs} was calculated to be 35 on $NH_4PMo_4W_8$ in 0.001 M HNO_3.

The effect of acidity on K_d at const. [NH_4^+] is practically negligible up to 2 M HNO_3, but at higher acidity K_d decreases.[(9)]

[(1)] W. J. O'LEARY and J. PAPISH, *Ind. Eng. Chem. Anal. Edit.* **6**, 107 (1934).
[(2)] M. H. FELDMAN and L. E. GLENDENIN, N.NES Part IV **9**, 654 (1951).
[(3)] H. BUCHWALD and W. P. THISTLETHWAITE, *J. Inorg. Nucl. Chem.* **5**, 341 (1958).
[(4)] J. VAN R. SMIT, J. J. JACOBS and W. ROBB, *J. Inorg. Nucl. Chem.* **12**, 95 (1959).
[(5)] J. KRTIL and V. KOUŘÍM, *J. Inorg. Nucl. Chem.* **12**, 367 (1960).
[(6)] J. KRTIL, *J. Inorg. Nucl. Chem.* **19**, 298 (1961).
[(7)] A. I. KOKORIN and N. A. POLOTEBNOVA, *Zh. Obshch. Khim.* **26**, 1 (1956).
[(8)] A. F. WELLS, *Structural Inorganic Chemistry* (2nd Ed.), Clarendon, Oxford (1950).
[(9)] J. KRTIL, *J. Inorg. Nucl. Chem.* **24**, 1139 (1962).

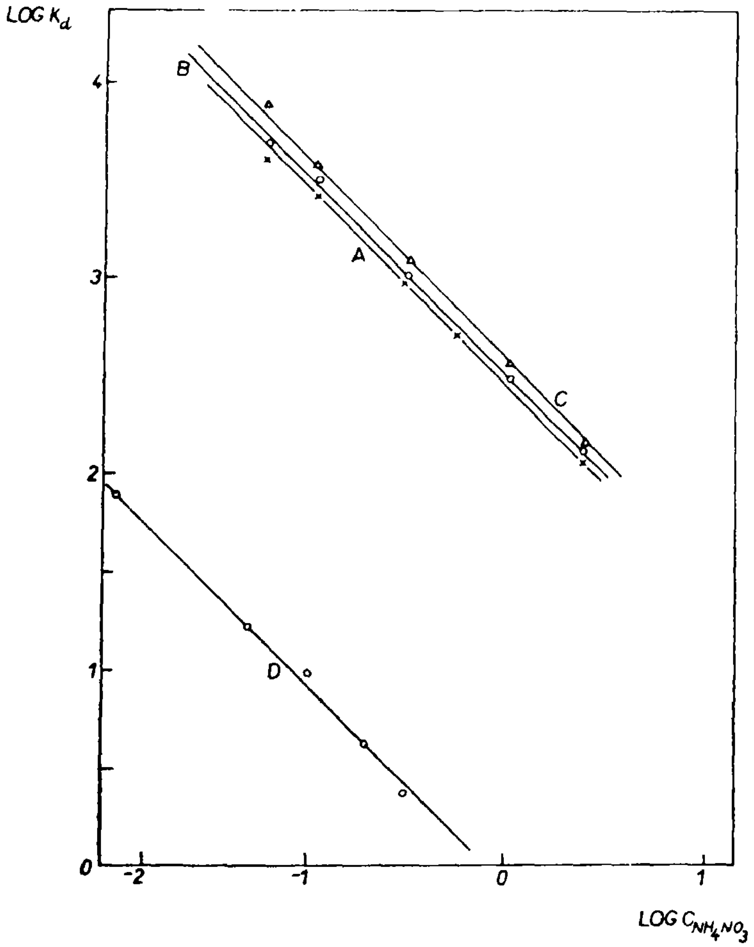


FIG. 1 —Dependence of the distribution coefficients K_d on equilibrium concentration of ammonium ions in the solution

A $NH_4PMo_4W_8$ B $NH_4PMo_6W_6$ C $NH_4PMo_8W_4$

A—C indicates Cs $[H^+]$ = [0,001 M]

D indicates Rb K_d ml/g

D - - - - indicates $NH_4PMo_4W_8$ $C_{NH_4NO_3}$ molarity of NH_4NO_3

Dynamic experiments

Microquantities of Cs and Rb were found to be sorbed in neutral media (0 4 M $NaNO_3$) and also in strong acids (12 M HCl, 12 M HNO_3) 1 M NH_4NO_3 elutes Rb quantitatively, and caesium can be eluted quantitatively with 10 M NH_4NO_3 Satisfactory results were also obtained with macro-amounts of Cs Figure 2 shows the separation of traces of Rb from Cs on $NH_4PMo_4W_8$ by elution with 1 M NH_4NO_3 followed by 10 M NH_4NO_3

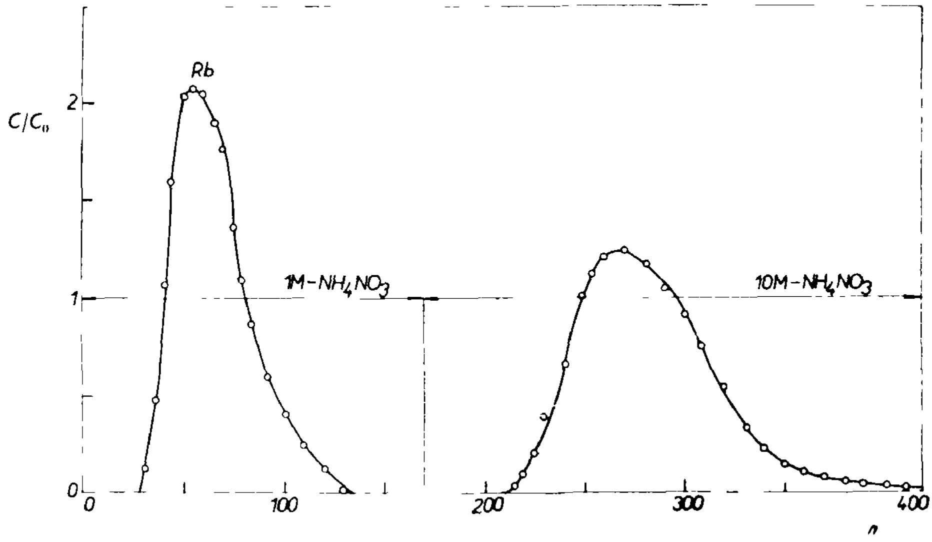


FIG 2 -Separation of trace ^{86}Rb from trace ^{137}Cs Column 1 13 cm² 12 cm, ion exchanger $NH_4PMo_4W_8$ bed- 3 cm, weight ratio $NH_4PMo_4W_8$ asbestos 1 1, drop interval 15 sec

C/C_0 volume per cent of alkali in 1 drop of eluate

n number of drops

Institute of Nuclear Research
Czechoslovac Academy of Sciences
Řež u Prahy

J KRTIL
I KŘIVÝ

Spectrophotometric and potentiometric investigations on Mn (iii)–1:8 dihydroxy naphthalene 3:6 disulphonic acid chelate

(*Received* 29 *April* 1963)

IN RECENT years the complexes of 1 8 dihydroxy naphthalene 3 6 disulphonic acid (chromotropic acid) have received considerable attention since many of them find uses in analytical chemistry SCHWARZENBACH[1] made a detailed study of the Fe(III) chelate while SOMMER[2] and coworkers carried out an extensive study of the Ti(IV) complexes and they have been used for the colorimetric estimation of Ti(IV) WARE[3] suggested the use of this reagent for the determination of uranium

Little has been done on the interaction of unstable oxidation states with chromotropic acid In the present communication the results of the interaction of chromotropic acid with Mn(III) described employing spectrophotometric and potentiometric methods

[1] J HELLER and G SCHWARZENBACH *Helv Chim Acta* **24**, 1876 (1951)

[2] A OKÁČ and L SOMMER, *Z anal Chem* **143**, 52 (1954) *Anal Chim Acta* **15**, 345 (1956)

[3] F WARE, U S A, E C Rep MDDC (1945)

Experimental

Manganic sulphate was prepared by a modification of UBBELOHDE's method(4) and the solution was stored in dark coloured bottles and the strength determined by titrating potentiometrically against ferrous ammonium sulphate E Merck reagent grade chromotropic acid (sodium salt) was used

The spectrophotometric measurements were made with a BAUSCH and LOMB Spectronic "20", while the potentiometric measurements were carried out with a PYE precision potentiometer (type 7568) using saturated calomel and platinum electrodes

The absorption spectra of the Mn(III) solution and Mn(III) D N S complex were measured(5) in the wave length range 350–600 mμ Mn(III) sulphate shows a single absorption peak at 515 mμ whereas the λ_{max} of the chelate was found to lie at 430 mμ

The composition of the complex was determined by (a) JOB's method of continuous variation(6) and (b) Slope ratio method (7) It was found that the complex was formed in the molar ratio Mn(III) D N S as 1 1 It was observed that above pH 1, the colour of the complex was completely destroyed, hence the extinction measurements could only be made in the presence of dilute sulphuric acid

The formation constant for the chelate was determined by the method recommended by MUKERJI and DEY(8) For two mixtures having the same optical density (0 20), the value of K came out to be $1\ 8 \times 10^{2}$ and the calculate value of ΔF° was found to be 3 11 K Cal

The reaction of Mn(III) sulphate with chromotropic acid was further investigated by potentiometric titration D N S solutions of varying concentration (1×10^{-2} M to 2×10^{-3} M) were titrated with 1×10^{-2} M Mn(III) The breaks in the curves agree with the ratio 1 1 for the complex The reverse titrations, however, did not prove successful since there were no significant breaks in the curves

Discussion

The complex may be represented as Mn^{III}(DNS) which may be formulated as a chelate complex The strong tendency of hydroxyl groups to form stable coordination complexes with metal is well known In the present case the development of a stable colour supports this viewpoint and the possibility of chelate ring structure being formed, is indicated

Potentiometric titration confirmed the conclusion arrived at by spectrophotometry

The formation of a stable coloured complex between Mn(III) and DNS in the highly acidic may be advantageously employed for the colorimetric determination of Mn(III) in small amounts Further work is in progress

Acknowledgements –The authors wish to express their thanks to Dr W U MALIK for his valuable criticism

ANEESUDDIN MALIK
S M FAZLUR RAHMAN

Prince of Wales Chemical Laboratories
Muslim University, Aligarh

(4) A R J P UBBELOHDE, *J Chem Soc* 1605 (1935)

(5) W C VOSBURGH and G R COOPER, *J Amer Chem Soc* **63**, 437 (1941)

(6) P JOB, *Ann Chim* **9**, (10), 113 (1928)

(7) E HARVEY and D L MANNING, *J Amer Chem Soc* **72**, 4488 (1950)

(8) A K MUKERJI and A K DEY, *Proc Natl Acad Sci , India* **26**, 20 (1957)

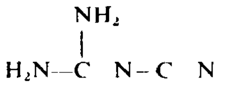
Dicyandiamide–copper(II) complexes and the metal ion catalysed addition of alcohols to a nitrile

(*Received* 29 *March* 1963)

IT HAS previously been reported(1) that copper (II) ion catalyses the addition of alcohols to the nitrile group in dicyandiamide (dcda), I, forming N^1-alkylguanylureas, II Thus if dicyandiamide is reflux in an alcohol in the presence of copper (II) acetate,

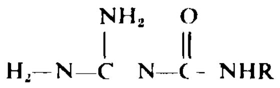
---

(1) R L DUTTA and P RÂY, *J Indian Chem Soc* **36**, 499 (1959)



$$H_2N{-}\overset{NH_2}{\overset{|}{C}}{=}N{-}C{\equiv}N$$

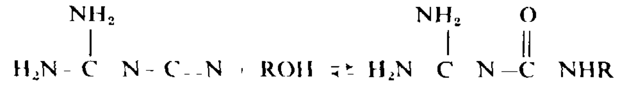
I



$$H_2N{-}\overset{NH_2}{\overset{|}{C}}{=}N{-}\overset{O}{\overset{\|}{C}}{-}NHR$$

II

the corresponding alkylguanylurea complex separates from the solution. Although the exact role of the metal in catalysing the reaction is not known, DUTTA and RÂY suggested that the following equilibrium existed



$$H_2N{-}\overset{NH_2}{\overset{|}{C}}{=}N{-}C{\equiv}N + ROH \rightleftharpoons H_2N{-}\overset{NH_2}{\overset{|}{C}}{=}N{-}\overset{O}{\overset{\|}{C}}{-}NHR$$

and the metal ion shifted the equilibrium toward the formation of product by removing the product through complexing. They were unable to obtain analogous results using Ni(II) ion and this they attributed to the fact that Ni(II) complexes less strongly with the product and is thus unable to shift the equilibrium.

We have two results to report which we feel are pertinent to this question. Nickel (II) although less effective than Cu(II) in catalysing the reaction, does do so. If nickel (II) chloride and dicyandiamide in a 1:2 ratio are placed in methanol and refluxed, after a period of about 3 hr bright orange crystals begin to deposit on the sides of the flask. Refluxing for several more hours yields large quantities of the crystals. The product was diamagnetic and very insoluble in water and methanol. The analysis agreed well with that expected for bis(N¹-methylguanylurea)-nickel (II) chloride. *Anal.* Calc. for $NiC_6N_8H_{16}O_2Cl_2$: C, 19.90; N, 30.86; H, 4.42. Found: C, 20.20; N, 30.68; H, 4.50%.

That the nickel is less effective as a catalyst than copper is shown by the relative rates at which the reaction takes place. While the reaction with nickel requires 3 hr under reflux conditions for observable reaction to take place, the copper catalysed reaction is observable after 2 hr at room temperature and after 4 hr at 0°. It is worth noting that if dicyandiamide is refluxed in methanol overnight in the absence of a metal ion there is no evidence of reaction as indicated by the lack of complex formation upon subsequent addition of Ni(II) or Cu(II).

The second fact which we wish to report is that dicyandiamide (dcda) itself forms complexes with Cu(II). If a saturated aqueous solution of $CuSO_4$ is mixed with a saturated aqueous solution of dicyandiamide in a 1:2 molar ratio and cooled at 0° for 15–20 min, a bulky blue precipitate forms. The precipitate is washed extensively with cold water and dried to constant weight in a vacuum at room temperature. The analysis agrees well with the formula $[Cu(dcda)_2]SO_4 \cdot 5H_2O$ (III). *Anal.* Calc. for $CuC_4N_8H_{18}SO_9$: Cu, 15.2; C, 11.50; H, 4.31. Found: Cu, 15.3; C, 11.50; H, 4.36%.

The blue complex shows the typical broad absorption band in the red region with λ_{max} being 775 mμ in water and 785 mμ in methanol. The magnetic moment is 1.87 B.M. at room temperature.

Since Cu(II) ion is also known to catalyse the addition of water to dicyandiamide to yield guanylurea,[2] we studied the infrared spectrum of the complex in order to assure that such a reaction had not occurred. The nitrile group in dicyandiamide has a doublet peak at about 4.5 μ[3] and this peak remains essentially unchanged in the complex, indicating that hydration had not taken place, presumably because of the immediate precipitation of the complex from solution.

If the blue complex, (III), is heated at 50° in a vacuum, a green product is obtained. The weight loss and the analysis correspond closely to $[Cu(dcda)_2]SO_4 \cdot 2H_2O$ (IV). *Anal.* Calc. for $CuC_4N_8H_{12}SO_6$: Cu, 17.4; C, 13.2; H, 3.3. Found: Cu, 17.2; C, 13.0; H, 3.5%.

The room temperature magnetic moment is 1.86 B.M. and λ_{max} is 750 mμ in methanol. The infrared spectrum also indicated that the nitrile group was essentially unchanged upon complex formation.

If either (III) or (IV) is refluxed in methanol for an hour, bis(N¹-methylguanylurea)copper (II) sulphate precipitates in the form of violet crystals. *Anal.* Calc. for $CuC_6N_8O_2H_{16}SO_4$: C, 18.4; N, 28.6; H, 4.08. Found: C, 18.5; N, 28.4; H, 4.26%. This is, as expected, the same as obtained by refluxing a mixture of dicyandiamide and copper (II) sulphate in methanol Qualitatively, however, we observe that the reaction is faster if we start with the complex

---

[2] P. RÂY, *Chem. Rev.* **61**, 313 (1961).

[3] L. J. BELLAMY, *The Infra-red Spectra of Complex Molecules*, Wiley, New York, 1958, p. 293.

We find a room temperature moment for bis(N^1-methylguanylurea)copper (II) sulphate of 1 84 B M Dutta and Rây report a value of 1 65 for the 3 5 hydrate of the same complex [4]

In view of the above results it seems to us that the metal ion plays a more significant role in the addition of alcohol to dicyandiamide than that proposed by Dutta and Rây We are currently investigating this reaction in an effort to elucidate the mechanism as well as testing the generality of the reaction

Acknowledgment -Support of this work by the National Science Foundation under Grant NSF 9-14529 is gratefully acknowledged

Department of Chemistry
Syracuse University
Syracuse 10 New York

W A Baker, Jr
M Daniels*

* National Science Foundation Undergraduate Research Participant

[4] R L Dutta and P Rây *J Indian Chem Soc* **36**, 567 (1959)

Half-lives of some rare earth nuclides*

(*Received* 8 *April* 1963)

Incidental to the investigation of various radiochemical problems, measurements of the half-lives of a number of rare-earth isotopes have been made Although some of the values are in agreement with other published results,(1 2 3 4) they have been included because confirmation of one of a number of existing values should be of help to other investigators in their choice of the best half-life

Experimental

Sample preparation

Those rare earth activities which were obtained from thermal neutron fission of ^{235}U were separated from the bulk of the fission products and uranium by a standard chemical procedure involving anion resin column steps, and lanthanum hydroxide and fluoride precipitations The individual rare earths were then separated from each other by elution from Dowex 50, X4 cation exchange resin columns with ammonium α-hydroxyisobutyrate solutions at room temperature [5] Initial purification of the gadolinium and terbium activities produced by thermal neutron irradiation of gadolinium oxide was accomplished by two or three lactate elutions from Dowex 50 resin columns to remove the mass of the gadolinium target material This was followed by further purification of the tracer amount of terbium activity by elution with α-hydroxyisobutyrate from a very small Dowex 50 resin column

The neutron irradiations of uranium Tb_2O_3, and Gd_2O_3 were done in the Los Alamos "Water Boiler" reactor, the long neutron irradiations of Dy_2O_3 and Gd_2O_3 were carried out in the Los Alamos Omega West Reactor

Counting and data analysis

The decay of all the samples was followed with gas flow, beta-proportional counters with 1 in or 2 in dia , 4 9 mg/cm^2 aluminum windows

A least-squares analysis of the data was performed by IBM 704 or 7090 computers The half-lives obtained from these calculations are summarized in Table 1 The errors quoted on the average

---

* This work was done under the auspices of the U S Atomic Energy Commission

[1] D F Peppard, G W Mason and S W Moline, *J Inorg Nucl Chem* **5**, 141 (1957)

[2] H W Wright, E I Wyatt, S A Reynolds, W S Lyon and T H Handley, *Nucl Sci Engng* **2**, 383 (1957)

[3] L R Bunney, J O Abriam and E M Scadden, *J Inorg Nucl Chem* **12**, 228 (1960)

[4] D Strominger, J M Hollander and G T Seaborg, *Rev Mod Phys* **30**, 585 (1958)

[5] H L Smith and D C Hoffman, *J Inorg Nucl Chem* **3**, 243 (1956)

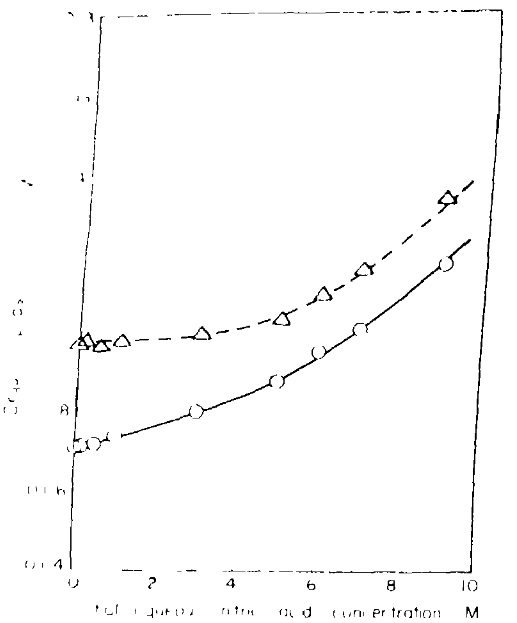


FIG. 2 Change in acidity of organic phase on extraction of uranium (VI) with 0 1 M DEHPA in kerosene (in the presence of uranium, Δ in the absence of uranium)

but increases steadily with increasing aqueous acidity over the whole range Below 3 M the change in acidity of the organic phase is analogous to that for extraction from sulphuric acid solution[1] but at higher acidities it is presumed that nitric acid is extracted into the organic phase together with uranyl nitrate as in the case of TBP[8]

In order to confirm this conclusion the extraction of acid from 6 M nitric acid was studied at varying DEHPA concentrations at 20°C, with the results shown in Fig 3 The slope of the line is nearly unity (1 1) and since DEHPA is predominantly present as the dimer in the organic phase this implies that each dimeric DEHPA combines with one molecule of nitric acid by the following reaction[9]

$$HNO_3(a) + (HX)_2(o) \rightleftarrows HNO_3\,(HX)_2(o) \qquad (9)$$

From Fig 2 we may compare the change in acidity in the organic phase with the organic phase uranium concentration In the absence of any other reaction in the organic phase two hydrogen ions are exchanged for each uranyl ion at low nitric acid concentrations, while one molecule of uranyl nitrate will displace two molecules of nitric acid extracted into the organic phase under suitable conditions at higher nitric acid concentrations It was found that below 3 M HNO_3 change in acidity in the organic solution corresponded approximately to twice the organic phase uranium concentration, and was less than the latter at above 3 M This confirms that DEHPA extracts uranium by an ion-exchange mechanism at low aqueous acidities, at highe acidities the extraction by DEHPA is more complicated than that with TBP,[10] sinc the ion-exchange reaction also occurs to some extent

---

[8] T SATO *J Inorg Nucl Chem* **9,** 188 (1959)

[9] B F GREENFIELD and C J HARDY, *J Inorg Nucl Chem* **21,** 359 (1961)

[10] T V HEALY and H A C MCKAY, *Trans Faraday Soc* **52,** 633 (1956)

Table 1.—Summary of decay data

Nuclide		Half-life	Method of production	Other components present*	Length of decay observation (days)
^{91}Y		58.8 ± 0.2 days (σ = 0.04 days)†	^{235}U (n, f)	none	389
^{143}Pr		13.55 days (σ = 0.01 days)	^{235}U (n, f)	none	5–100 after bombardment
		13.62 days (σ = 0.01 days)	^{235}U (n, f)	none	5–118 after bombardment
	Average	13.59 ± 0.10 days			
^{144}Pr		17.28 min (σ = 0.08 min)	milked from ^{144}Ce	0.2% long-lived	0.5
		17.31 min (σ = 0.03 min)	milked from ^{144}Ce	0.2% long-lived	0.5
	Average	17.30 ± 0.05 min			
^{147}Nd		11.015 days (σ = 0.003 days)	^{235}U (n, f)	^{147}Pm daughter	201
		11.019 days (σ = 0.008 days)	^{235}U (n, f)	^{147}Pm daughter	239
	Average	11.02 days ± 0.05 days			
^{149}Pm		53.07 ± 0.10 hr (σ = 0.02 hr)		~5 × 10^{-3}% of a long comp (^{147}Pm?)	64
^{151}Pm		27.8 ± 0.5 hr (σ = 0.14 hr)	^{235}U (n, f)		
^{153}Sm		46.5 ± 0.5 hr (σ = 0.3 hr)	^{235}U (n, f)	9 hr ^{156}Sm and 15 day ^{156}Eu daughter (0.5%)	96
^{153}Gd		242 ± 1 days (σ = 0.17 days)	^{152}Gd (n, γ) in natural Gd	none	6–490 after bombardment
^{160}Tb		72.18 days (σ = 0.05 days)	^{159}Tb (n, γ)	~2% ^{161}Tb	1–468 after bombardment
		71.99 days (σ = 0.06 days)	^{159}Tb (n, γ)	~7% ^{161}Tb	32–461 after bombardment
	Average	72.1 ± 0.3 days			
^{161}Tb		6.89 days (σ = 0.02 days)	^{160}Gd (n, γ) ^{161}Gd $\xrightarrow{\beta^-}$ ^{161}Tb in natural Gd	0.3% ^{160}Tb	91
		6.86 days (σ = 0.02 days)		0.5% ^{160}Tb (formed by (n, γ) on ^{159}Tb in the Gd)	87
	Average	6.88 ± 0.10 days			
^{159}Dy		151 ± 2 days (σ = 0.80 days)	Dy (n, γ)	^{166}Dy — ^{166}Ho, 0.1% of 30 yr ^{166}Ho	10–567 after separation from Ho
^{166}Dy		81.43 hr (σ = 0.04 hr)	Dy (n, γ)^2 75 day irradiation	~0.2% ^{159}Dy, 27 hr ^{166}Ho daughter and 2 × 10^{-4}% of 30 yr ^{166}Ho	10–37 after separation from Ho
		81.64 hr (σ = 0.05 hr)			10–41 after separation from Ho
		81.35 hr (σ = 0.04 hr)			10–567 after separation from Ho
	Average	81.46 ± 0.20 hr			
^{166}Ho		27.0 ± 0.2 hr (σ = 0.08 hr)	milked from ^{166}Dy	none	14

* The reported intensities are corrected to the end of bombardment

† The values for σ given in parentheses are the standard deviations obtained from the least squares analysis of the counting data, the errors quoted for the averages are estimated over all errors

half-life values are estimated overall errors based on the standard deviations obtained from the least-squares analysis the number of separate half-life determinations and the length of time the decay was followed

Acknowledgements The author gratefully acknowledges the assistance of Mrs Francine O Lawrence with the data analysis, and the cooperation of the Los Alamos reactor group in providing the irradiations

D C Hoffman

University of California
Los Alamos Scientific Laboratory
Los Alamos, New Mexico

The preparation and some properties of molybdenum (V) oxotrichloride

(*Received* 4 *May* 1963)

Standard texts(1) on non-aqueous solvents state that tungsten (VI) chloride is solvolysed by liquid sulphur dioxide giving the oxotetrachloride, yet report that the somewhat more reactive chloride of the same transition group molybdenum (V) chloride, does not react It is known, however, that this halide can abstract oxygen from ligands such as dimethylsulphoxide to form complexes of the type $MoOCl_3$, 2L(2) and will also give oxotetrachloromolybdates (V) with alkali metal chlorides in liquid sulphur dioxide (3) It was therefore felt that a further examination of the $MoCl_5$–SO_2 system might indicate the formation of molybdenum (V) oxotrichloride, which until now has only been prepared by the high temperature reaction of the pentachloride with the trioxide *in vacuo* (4) This method has, however, been found to be inconvenient as several separations *in vacuo* are essential to remove large amounts of the oxotetrachloride and dioxodichloride also formed It was hoped that in sulphur dioxide only the oxotrichloride would be formed

The reaction was studied under rigorously anhydrous conditions in an all-glass vacuum system An excess (50 ml) of sulphur dioxide previously dried by several distillations from phosphoric oxide, was distilled on to resublimed molybdenum (V) chloride (1–2 g) in an ampoule at 78 , the ampoule sealed and kept at room temperature for at least one week when a dark brown solid and solution formed The ampoule was then opened under dry nitrogen, the excess of sulphur dioxide distilled off and the solid remaining pumped at 100 to remove possible solvates and sulphur oxychlorides Found Mo, 44 3, Cl, 48 4%, Mo Cl O (diff) 1 00 2 96 0 99 $MoOCl_3$ requires Mo, 44 0, Cl 48 6%

The product was instantly attacked by moist air, hydrolysed by water to give a brown solution, soluble in dry methanol with alcoholysis, soluble in dry acetone, but insoluble in non-polar solvents such as benzene The green acetone solution showed peaks in the visible region of the spectrum at 13700 (ε - 20) and 22200 (ε 20) cm^{1} The product was also soluble in 10 M hydrochloric acid with the formation of the $[MoOCl_5]^{2}$ ion, isolated as the caesium salt by addition of caesium chloride Found Mo, 17 2, Cl, 32 2, Cs, 47 8% Cs_2MoOCl_5 requires Mo, 17 3, Cl, 32 0, Cs, 47 9% The visible spectrum of the $[MoOCl_5]^{2}$ ion was measured for comparison with the acetone solution, peaks occurring at 14100 (ε 15) and 22400 (ε 10) cm^{1} In the infra-red region the product showed a medium-strong band at 1020 cm^{1} compared with a strong band at 970 cm^{-1} for the Cs_2 $MoOCl_5$, these peaks being in the range which has been assigned to the Mo O stretching frequency (5)

A valence state determination, by dissolving the product in excess of cerium (IV) sulphate solution and back-titrating with iron (II) ethylenediammonium sulphate, showed a "change" with respect to sexivalent molybdenum of 1 05 units The magnetic moment of a finely powdered sample, using a Gouy apparatus was 1 62 B M at 295 A

(1) L F Audrieth and J Kleinberg, *Non-aqueous solvents*, Wiley, New York, 1953

(2) S M Horner and S Y Tyree Jr , *Inorg Chem* 1, 122 (1962)

(3) E Allen, private communication

(4) I A Glukhov and S S Eliseev, *Zh Neorg Khim* 7, 81 (1962)

(5) C G Barraclough, J Lewis and R S Nyholm, *J Chem Soc* 3552 (1959)

It is clear therefore that molybdenum (V) chloride can abstract oxygen from sulphur dioxide to form the oxotrichloride, the valence state determination and magnetic moment, although it is slightly reduced, both being indicative of quinquevalent molybdenum The structure of the oxychloride is likely to be similar to that of niobium oxotrichloride[(6)] with trans-octahedral MoO_2Cl_4 groups linked into double chains by sharing two chlorines at an edge and oxygen atoms at two opposite vertices, the slight reduction of the magnetic moment from the "spin-only" value (also shown by $MoCl_5$,[(7)]) being due to a weak coupling of electron spins of neighbouring molybdenum atoms The compound would thus easily give in hydrochloric acid the $[MoOCl_5]^{2-}$ ion and in acetone, $MoOCl_3$, $2(CH_3)_2CO$ It is apparent that a monomeric octahedral complex is formed in acetone since the visible spectrum is so similar to that of the $[MoOCl_5]^{2-}$ ion in which a strong tetragonal distortion of the octahedral species occurs, the spectral features being given by the MoO^{3+} ion, the other ligands lowering the field symmetry insignificantly[(8, 9)] In both cases the transitions of the single unpaired electron will be $B_{2g} \rightarrow E_g$ and $B_{2g} \rightarrow B_{1g}$

Acknowledgements- I wish to thank Dr G W A Fowles of the University of Southampton for the use of the Gouy Balance and the Climax Molybdenum Co for the gift of molybdenum (V) chloride

D A Edwards

Department of Chemistry and Biology
Bristol College of Science and Technology
Ashley Down
Bristol 7

---

(6) D E Sands, A Zalkin and R E Elson, *Acta Cryst* **12**, 21 (1959)
(7) K Knox and C E Coffey, *J Amer Chem Soc* **81**, 5 (1959)
(8) C K Jorgensen, *Acta Chem Scand* **11**, 73 (1957)
(9) H B Gray and C R Hare, *Inorg Chem* **1**, 363 (1962)

J. Inorg. Nucl. Chem. 1963 Vol. 25 p. 1200 Pergamon Press Ltd. Printed in Northern Ireland

ERRATA

TAICHI SATO: The extraction of uranium(VI) from sulphuric acid solutions by tri-n-dodecylamine. *J. Inorg. Nucl. Chem.* **24,** 1267–1276 (1962)

Page 1273, Figure 8

for "Frequency, M" read "Frequency, cm^{-1}"

A. LIBERTI, V. CHIANTELLA and F. CORIGLIANO: Mononuclear hydrolysis of titanium (IV) from partition equilibria, *J. Inorg. Nucl. Chem.* **25,** 415–427 (1963)

Page 426, equation (10)

for "K_x = $[Ti(OH)_x]^{(4-x)}$ $[OH^-]^x$" read "$K_x = [Ti(OH)_x^{(4-x)}]$ $[OH^-]^x$"

Page 426, line 6 after equation (10),

for "$[TiOH^{3+}][OH^-]^3 = 10^{9\cdot4}$" read "$K_1 = [TiOH^{3+}][OH^-]^3 = 10^{-9\cdot4}$"

J Inorg Nucl Chem 1963 Vol 25, pp 1201 to 1211 Pergamon Press Ltd Printed in Northern Ireland

RELATIVE YIELDS OF THE PAIRS ^{95g}Nb–^{95m}Nb AND ^{96}Nb–^{95}Nb IN FISSION OF Pb, Bi, Th AND U INDUCED BY 15–157 MeV PROTONS

EINAR HAGEBØ
The Gustaf Werner Institute, University of Uppsala, Uppsala, Sweden

(*Received* 30 *December* 1962 *in revised form* 22 *February* 1963)

Abstract -The ratio between the fission yield of the high spin isomer and that of the low spin isomer has been measured for the isomeric pair ^{95g}Nb-^{95m}Nb as a function of the irradiation energy and of the target used For all the targets used, the isomeric yield ratio increases with increasing proton energy, and for a given irradiation energy, the ratio is highest when lead is irradiated and lowest when uranium is irradiated A simple statistical model calculation indicates that the spin of the primary fission fragment produced by the fission of uranium is very low for low bombarding energies

In the same experiments the ratio between the fission yields of 24 hr ^{96}Nb and ^{95}Nb has been measured

THE study of relative yields of isomers has been, for some time, a way of gaining information about angular momentum transfer and conservation, particularly in more simple nuclear reactions than fission

Only very few data have been collected on relative yields of isomers produced by charged particle induced fission, and most of the work has been concentrated on the ^{115}Cd-isomers, which have not yet given an independent yield ratio as the precursor half life is too short (1) BAILEY(2) gives a review of literature up to 1959, including work done both on fission products and on spallation products Some later studies on isomeric yield ratios from ordinary nuclear reactions can be found among the references (3-9) HALLER and ANDERSSON(9) have even studied the yield ratio ^{80m}Br/^{80g}Br from proton induced fission of uranium

Parallel to the present work the yield ratio ^{95g}Nb/^{95m}Nb produced by proton bombardment of uranium have been studied by ABECASIS *et al* (10) in Oslo, using a different approach, as well in chemical technique, as in counting technique

(1) *Nuclear Data Sheets*, National Academy of Sciences National Research Council, Washington D C

(2) S M BAILEY, Report UCRL-8710 (1959)

(3) S ABECASIS and S NASSIFF, Informe No 38 (1960), Comision Nacional de Energia Atomica, Argentina

(4) J R HUIZENGA and R VANDENBOSCH, *Phys Rev* **120,** 1305 (1960)

(5) R VANDENBOSCH and J R HUIZENGA, *Phys Rev* **120,** 1313 (1960)

(6) S J NASSIFF and H VIGNAN, Informe No 53 (1961), Comision Nacional de Energia Atomica, Argentina

(7) S J NASSIFF, S ABECASIS and A MOCOROA, Informe No 61 (1961), Comision Nacional de Energia Atomica, Argentina

(8) I B HALLER and G RUDSTAM, *J Inorg Nucl Chem* **19,** 1 (1961)

(9) I B HALLER and G ANDERSSON, *J Inorg Nucl Chem* **20,** 12 (1961)

(10) S ABECASIS R HESBØL, A C PAPPAS and R RADICELLA, Private communication (1962)

Quantitative theoretical predictions based on a statistical model, have been shown to fit experimental yield ratios from simpler nuclear reactions well,(4,5) but no attempts have been made to explain the fission results quantitatively, only qualitative suggestions are forwarded.

However, one would imagine that these isomeric yield ratios give some information about the spin distribution of the primary fission fragments. From a series of experiments(11) we know with a high degree of accuracy the average number of neutrons emitted from the fission fragments, the average energy of these neutrons and also the number and energy of prompt γ-rays following the neutron emission.(11) Using a statistical model(1,5,12) one can from these data calculate the expected yield ratio from a given spin of the primary fission fragment. It is expected that a statistical model should apply particularly well to fission fragments if the fission takes place at an energy far from the threshold. The exact form of the spin distribution is unknown, but at least for small values of the angular momentum, the distribution may be well represented by its average value. Following VANDENBOSCH and HUIZENGA(5) one can from a fragment characterized only by its spin, calculate the ratio between the isomers of the final fission product by the use of the above mentioned information as neutron- and γ-ray-energies and multiplicities.

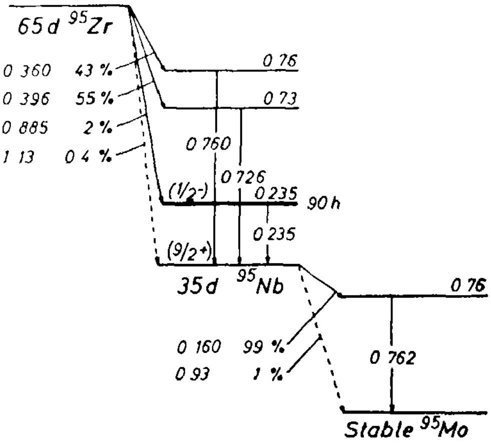


Fig. 1. Decay schemes of ^{95}Zr and ^{95}Nb, reproduced from reference (1) with details irrelevant for the present work omitted.

The main purpose of the present work is to study the isomeric yield ratio ^{95g}Nb/^{95m}Nb as a function of proton energy and target element, and to see if it is possible to gain some information on the order of magnitude of the angular momenta of the fission fragments using the above mentioned calculations.

The ratio ^{96}Nb/^{95}Nb was intended to be a study of charge distribution, but it is also useful in testing the reliability of the isomeric yield ratios.

The decay schemes of importance for this work are shown in Fig. 1.(1) In the following, "the isomeric yield ratio", will refer to the ratio $^{95g}\mathrm{Nb}\left(\frac{9}{2}+\right)\Big/{}^{95m}\mathrm{Nb}\left(\frac{1}{2}-\right)$ unless otherwise stated.

---

(11) J. HALPERN, *Ann. Rev. Nucl. Sci.* **9**, 245 (1959) (Review).

(12) T. ERICSON, *Phil. Mag. Suppl.* **9**, 425 (1960).

EXPERIMENTAL TECHNIQUE

Targets and irradiations. The targets used and their chemical form are shown in Table 1 together with irradiation energies used for the particular target. The thorium dioxide, bismuth and lead targets were made from Johnson Matthey "specpure" chemicals while the uranium trioxide was prepared from Merck's reagent grade uranylnitrate hexahydrate using a method described by PAPPAS.(13)

TABLE 1. IRRADIATION DATA

Target element	Target material	Bombarding energy (MeV)		Number of bombardments
		Max	Average	
Pb	Metal pieces	65	57	3
		90	80	3
		115	104	3
		140	128	2
		170	157	2
Bi	Metal pieces	65	57	3
		90	80	2
		115	104	3
		140	128	2
		170	157	2
Th	ThO_2 powder	50	43	2
		65	57	3
		90	80	2
		115	104	4
		140	128	2
		170	157	2
U	UO_3 powder	20	15	2
		35	29	3
		50	43	2
		65	57	2
		90	80	3
		115	104	5
		140	128	3
		170	157	7

The targets were all irradiated for one hour in the circulating proton beam of the synchro-cyclotron at the Gustaf Werner Institute.

Sample preparation. UO_3 was dissolved in conc. HNO_3, ThO_2 in conc. HNO_3 with some drops of 0.1 M $(NH_4)_2SiF_6$ added, Bi in conc. HNO_3 and Pb in 6 M HNO_3. In all cases 1 mg Nb-carrier in oxalic acid was added to the solvent together with about 1 mg amounts of Zr, Te (IV), Te (VI) and Mo holdback carriers.

$Nb_2O_5 \cdot xH_2O$ was precipitated from about 6 M HNO_3 by boiling and addition of $KBrO_3$. After dissolving the precipitate in hydrofluoric acid and performing two $BaZrF_6$ and LaF_3 scavengings from 3 M HF, $Nb_2O_5 \cdot xH_2O$ was precipitated using H_3BO_3 and NH_4OH. The precipitate was dissolved in 11 M HCl and niobium extracted with a solution of 7 per cent tribenzylamine in chloroform. Niobium was stripped from the organic phase using 6 M HCl, and precipitated as hydroxide with NH_4OH. The hydroxide was dissolved in one drop of hydrofluoric acid, transferred to a VYNS film of about 0.1 mg/cm^2 thickness and evaporated to dryness under a heating lamp.

---

(13) A. C. PAPPAS, AECU-2806, MIT-LNS-63 (1953). (Inaugural Dissertation, University of Oslo).

To minimize the influence of growth of ^{95}Nb from 65 day ^{95}Zr, the first precipitation of hydrated niobium oxide was performed 10–15 min after the end of irradiation It was shown that in the presence of carrier zirconium is not precipitated together with niobium under the conditions of the experiment As the problem in this work consisted of determining relative yields, the chemical yield was not determined, but is known[14] to be of the order of 30 per cent After about one month the purity of the samples was checked by measuring γ-spectra using a Hilger and Watts 3 in × 3 in NaI(Tl) crystal and a RIDL 400 channel pulse-height analyser A few samples showing low γ-activities not belonging to the decay of ^{95}Nb were discarded The others were counted for a time between three and seven months The impurities in the samples counted amounted to less than 0 01 per cent

Determination of relative yields The samples were counted in a flow proportional counter with a thin window (250 μg/cm^2) Unfortunately, low activities on many of the samples necessitated long counting times to obtain a reasonable number of counts ($\sim$ 5000) and this led to few points on the decay curves for about one third of the samples, with accompanying greater uncertainties in the resolution

Resolution of the decay curves was done graphically and the results corrected in a standard way[14] using correction factors given by RUDSTAM[15] PAPPAS[13] and NERVIK and STEVENSON[16] An internal conversion coefficient of 3 3[17, 18] was used for the 231 keV internal transition from ^{95m}Nb

Extrapolated values of the activities at the end of irradiation are obtained from the decay curves If A refers to ^{95m}Nb, B to ^{95g}Nb and C to ^{96}Nb, the following equations are valid for the corrected activities

$$D_A^{extr} = \frac{\lambda_A - 2\lambda_B}{\lambda_A - \lambda_B} R y_A (1 - e^{-\lambda_A T}) \tag{1}$$

$$D_B^{extr} = \frac{R}{\lambda_A - \lambda_B} [(\lambda_A - \lambda_B)(y_i)_B + \lambda_A y_A](1 - e^{-\lambda_B T}) \tag{2}$$

$$D_C^{extr} = R y_C (1 - e^{-\lambda_C T}) \tag{3}$$

In the above equations, D_B^{extr} is the value obtained by making a linear extrapolation of the 35 day slope of the ^{95g}Nb decay back to the end of irradiation, and D_A^{extr} by subtracting this curve from the observed sum of the ^{95m}Nb and ^{95g}Nb activities

$\lambda_{A, B, C}$ are decay constants, R is the fission rate, y_A $(y_i)_B$ and y_C are the fission yields of A, B and C, and T is irradiation time From these equations the two ratios $(y_i)_B/y_A$ and $y_C/y_A + (y_i)_B$ are calculated

The amount of ^{95}Nb grown from ^{95}Zr during irradiation and before the chemical separation of the two elements, has been neglected, as it can be calculated to be less than 0 01 per cent of the ^{95}Zr yield

EXPERIMENTAL RESULTS

The yield ratios ^{95g}Nb/^{95m}Nb and ^{96}Nb/$^{95(m+g)}$Nb are given in Table 2

The differences between the errors quoted for the isomeric yield ratio and for the ratio between ^{96}Nb and ^{95}Nb indicate the difficulties encountered in the graphical resolution of the decay curves The latter procedure is expected to be responsible for almost all of the uncertainties in the results as most of the counting correction factors cancel in the ratios

Figs 2–5 show the variation in the isomeric yield ratio ^{95g}Nb/^{95m}Nb and the ratio ^{96}Nb/^{95}Nb as functions of the bombarding energy for the four different targets used

---

[14] E HAGEBØ Unpublished results (1958)

[15] G RUDSTAM, Inaugural Dissertation, Uppsala (1956)

[16] W E NERVIK and P C STEVENSON, *Nucleonics* 10, No 3, 18 (March 1952)

[17] L A SLIV and I M BAND, *Coefficients of Internal Conversion of γ Radiation*, Academy of Sciences of the U S S R Moscow-Leningrad (1956)

[18] M E ROSE, *Internal Conversion Coefficients*, North Holland, Amsterdam (1958)

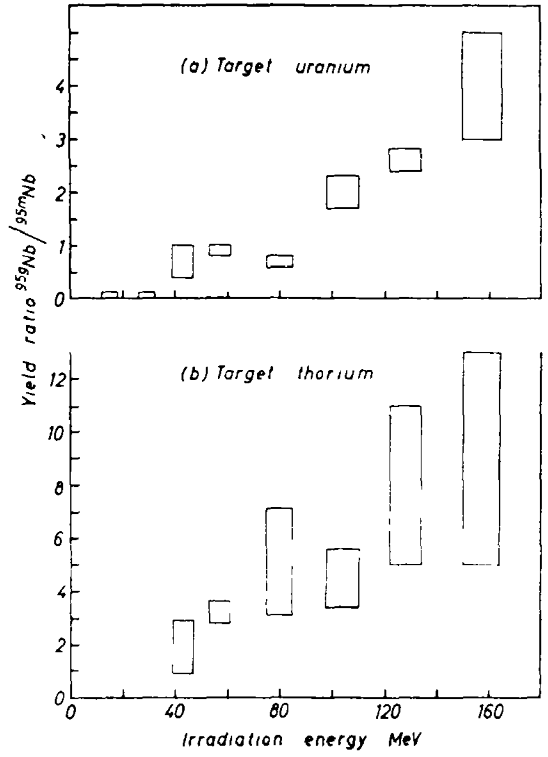


Fig. 2 Yield ratio ^{95g}Nb/^{95m}Nb vs irradiation energy from targets uranium and thorium

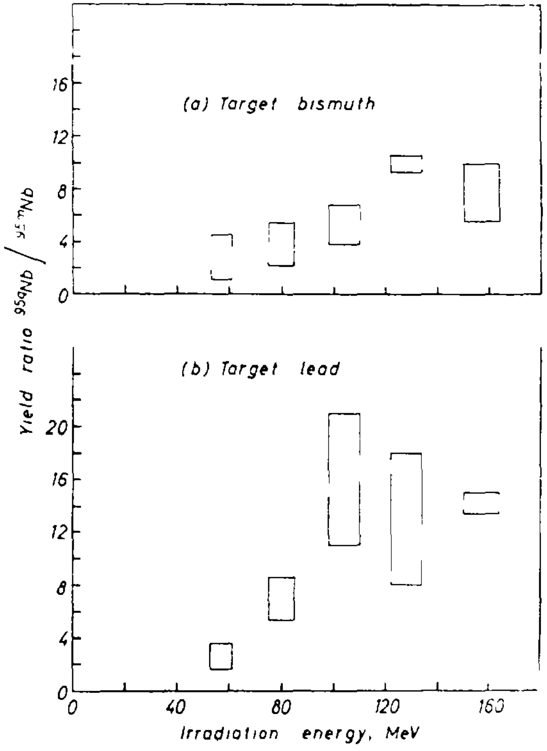


Fig 3 —Yield ratio ^{95g}Nb/^{95m}Nb vs irradiation energy from targets bismuth and lead

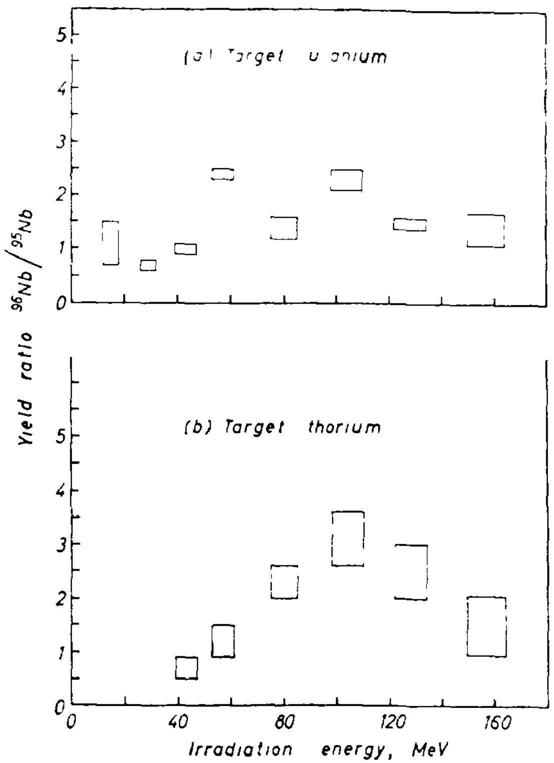


FIG 4 —Yield ratio $^{96}Nb/^{95}Nb$ vs irradiation energy from targets uranium and thorium

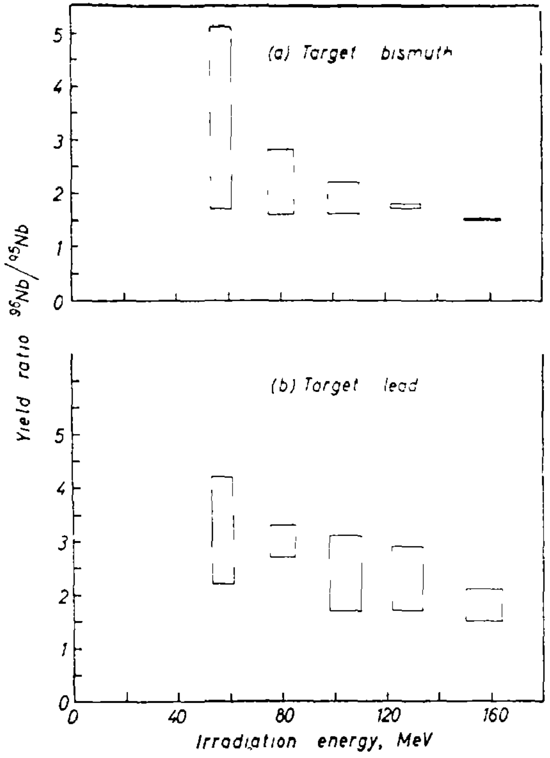


FIG 5 —Yield ratio $^{96}Nb/^{95}Nb$ vs irradiation energy from targets bismuth and lead

TABLE 2.—EXPERIMENTAL YIELD RATIOS

Target	Irradiation energy in MeV	$y(^{95g}\mathrm{Nb})/y(^{95m}\mathrm{Nb})$	$y(^{96}\mathrm{Nb})/y(^{95}\mathrm{Nb})$
Pb	57 ± 4	2.6 ± 1.0	3.2 ± 1.0
	80 ± 5	7.0 ± 1.6	3.0 ± 0.3
	104 ± 6	16.0 ± 5.0	2.4 ± 0.7
	128 ± 6	13.0 ± 5.0	2.3 ± 0.6
	157 ± 7	14.2 ± 0.8	1.8 ± 0.3
Bi	57 ± 4	2.8 ± 1.7	3.4 ± 1.7
	80 ± 5	3.8 ± 1.6	2.2 ± 0.6
	104 ± 6	5.3 ± 1.5	1.9 ± 0.3
	128 ± 6	9.9 ± 0.6	1.75 ± 0.04
	157 ± 7	7.7 ± 2.2	1.61 ± 0.01
Th	43 ± 4	1.9 ± 1.0	0.7 ± 0.2
	57 ± 4	3.2 ± 0.4	1.2 ± 0.3
	80 ± 5	5.1 ± 2.0	2.3 ± 0.3
	104 ± 6	4.5 ± 1.1	3.1 ± 0.5
	128 ± 6	8.0 ± 3	2.5 ± 0.5
	157 ± 7	9.0 ± 4	1.5 ± 0.6
U	15 ± 3	0.06 ± 0.07	1.1 ± 0.4
	29 ± 3	0.05 ± 0.05	0.7 ± 0.1
	43 ± 4	0.7 ± 0.3	1.0 ± 0.1
	57 ± 4	0.9 ± 0.1	2.4 ± 0.1
	80 ± 5	0.7 ± 0.1	1.4 ± 0.2
	104 ± 6	2.0 ± 0.3	2.3 ± 0.2
	128 ± 6	2.6 ± 0.2	1.5 ± 0.1
	157 ± 7	4.0 ± 1.0	1.4 ± 0.3

CALCULATIONS

The statistical model used by HUIZENGA and VANDENBOSCH(4,5) has been used to calculate the isomeric yield ratio ^{95g}Nb/^{95m}Nb resulting from an excited ^{96}Nb nucleus emitting one neutron and four γ-rays. The number of neutrons and γ-rays used is taken from the compilation of HALPERN.(11) An underlying assumption is that the fissioning nucleus already has evaporated as many neutrons as energetically possible and that the fission is accompanied by about the same number of neutrons from the fragments as in thermal neutron fission of heavy nuclei. This assumption is supported experimentally for uranium, e.g. by the work of HARDING and FARLEY(19) who found about 2.5 neutrons after fission when uranium was bombarded with 147 MeV protons. Concerning the other fissioning nuclei the assumption is somewhat doubtful.

The relative probability for a fragment with angular momentum J_c to emit a neutron with orbital angular momentum l leading to a final state with angular momentum J_f is given by

$$P(J_f) \propto \rho(J_f) \sum_{S=|J_f-\frac{1}{2}|}^{J_f+\frac{1}{2}} \; \sum_{l=|J_c-S|}^{J_c+S} T_l(E) \tag{4}$$

---

(19) G. N. HARDING and F. J. M. FARLEY, *Proc. Phys. Soc.* A **69**, 330 (1956).

where $T_l(E)$ is the barrier transmission coefficient for a neutron with orbital angular momentum l and energy E $\rho(J_f)$ is a theoretical level density factor given by(20,21)

$$\rho(J_f) \quad \rho(0)(2J_f + 1) \exp\left[-(J_f + \tfrac{1}{2})^2/2\sigma^2\right] \tag{5}$$

where $\rho(J_f)$ is the density of levels with spin J_f, $\rho(0)$ is the density of levels with zero spin and σ is the parameter characterizing the distribution function σ^2 is actually given by $\mathcal{J}T/\hbar^2$ where $\mathcal{J}$ is the nuclear moment of inertia and T the nuclear temperature (12) Considering only dipole radiation, the relative probabilities for a nucleus of spin J to decay to states with $J - 1$, J and $J + 1$ is determined by the level density factor $(2J_f + 1) \exp\left[\ (J_f + \tfrac{1}{2})^2/2\sigma^2\right]$

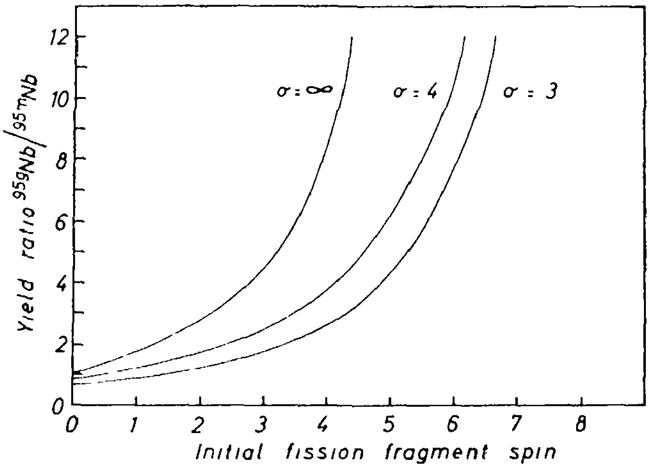


FIG 6—Calculated yield ratio ^{95g}Nb/^{95m}Nb vs, assumed initial fission fragment spin, for three different values of the parameter σ

The transmission coefficient $T_l(E)$ in Equation (4) is taken from FELD *et al*,(22) and three values, 3, 4 and ∞ have been used for the parameter σ in Equation (5) σ has been so chosen because $\sigma = 4 + 1$ is shown to fit a large number of experimental data quite well(1,5,23,24,25) and $\sigma = \infty$ has been used by a number of other authors in attempts to fit experimental results of isomeric yield ratios from different spallation reactions (see e g references 2 and 7)

The resulting isomeric ratios as a function of the initial spin of the fission fragment are shown in Fig 6 for the three choices of σ

These calculations are not expected to give clear-cut evidence either to what is the spin of the fission fragments or to what magnitude of σ^2 fits best. One was only looking for approximate values for the fission fragment spin, and it is realised that this could in this way only be achieved for the lowest isomer ratios Postulating any

---

(20) H A BETHE, *Revs Mod Phys* **9**, 84 (1937)

(21) C BLOCH, *Phys Rev* **93**, 1094 (1954)

(22) B T FELD, H FESHBACH, M L GOLDBERGER, H GOLDSTEIN, V F WEISSKOPF, NYO-636 (1951)

(23) T ERICSON, *Nucl Phys* **11**, 481 (1958)

(24) T ERICSON and V M STRUTINSKI, *Nucl Phys* **8**, 284 (1958)

(25) A C DOUGLAS and N MACDONALD, *Nucl Phys* **13**, 382 (1959)

kind of distribution for the fragment spin will lead to curves having a higher starting point and a smaller slope This has recently been done by WARHANEK and VANDENBOSCH[26] in a study of the isomeric yield ratio ^{135m}Cs/^{135g}Cs produced by thermal neutron fission of ^{235}U

DISCUSSION

The ratio ^{95g}Nb/^{95m}Nb Figs 2 and 3 show that the ratio between the high spin isomer and the low spin isomer is small when the bombarding energy is low, and that it increases with increasing bombarding energy The result is in agreement with the ^{80m}Br(5–)/^{80g}Br(1+) ratio studied by HALLER and ANDERSSON[9] The results from the work of ABECASIS *et al*[10] are also in excellent agreement with the present work, which is in disagreement with an earlier work by JODRA and SUGARMAN[27] on the ^{95}Nb isomers However, as the bombardments even at the highest energy used, to some extent lead to the formation of a compound nucleus,[28] the above results are expected from several reasons

(a) The angular momentum brought in by the incoming proton increases strongly with energy

(b) The nucleons evaporated from the compound nucleus are not expected to lower the average angular momentum to any appreciable extent, but merely serve to broaden the angular momentum distribution If the nucleus fissions before evaporation of neutrons, the same reasoning applies to the neutron evaporation from fission fragments

(c) From (a) and (b) follows that the fissioning nucleus will have an average angular momentum that increases with increasing bombarding energy Studies of angular distributions of fission fragments have shown that a great deal of this angular momentum goes into orbital motion, but as energy is raised, more appears as intrinsic spin of the fragments

The flattening of the curves at the high energies, indicated in Fig 3, is easily explained as due to competition from direct reactions, which do not bring in so much angular momentum to the resulting nucleus, but could also be due to the spin cutoff factor σ^2, which forces evaporating neutrons to take away appreciable amounts of angular momentum when this is very high

Recently GROVER[29] has pointed out, however, that γ-emission is a serious competitor to neutron emission when the angular momentum is high, following from the fact that when a nucleus decays by neutron emission it looses much energy and very little angular momentum The level density for high spin states in the energy region reached after neutron emission, may be very low and so the neutron decay will be highly forbidden even though it is energetically allowed This picture applies well to the fission fragments, but if we follow this line of thinking, we have to consider three competing processes, i e neutron emission, fission and γ-emission, in the original compound nucleus The prediction of results is thus made more difficult

[26] H WARHANEK and R VANDENBOSCH Personal communication from R VANDENBOSCH (1962)

[27] L G JODRA and N SUGARMAN, *Phys Rev* **99**, 1470 (1955)

[28] N METROPOLIS, R BIVINS, M STORM, A TURKEVICH, J M MILLER and G FRIEDLANDER, *Phys Rev* **110**, 185 (1958)

[29] J R GROVER, *Phys Rev* **123**, 267 (1961), **127**, 2142 (1962)

Comparing Figs 2 and 6 considering the calculations to be valid, the angular momentum of the uranium fission fragments have to be very small At this point it may be stated that if the ratios contain any contribution from the decay of ^{95}Zr, a correction for this contribution will make the ratios even smaller

COHEN *et al*(30) have studied the angular distribution of fragments from fission of uranium with 22 MeV protons According to their result, an appreciable amount of the total angular momentum becomes intrinsic spin of the fragments They measured, however only average anisotropies for each mass number, and it may well be possible that an improbable nucleus like ^{95}Nb is formed in a process different from the average one To be able to see if this reasoning is plausible, one experiment that we should like to see is a study of angular distributions of shielded nuclei This will probably also tell us something about the division between the fragments of the vector K, the projection of the total angular momentum I of the fissioning nucleus on the symmetry axis

The fission of thorium, bismuth and lead give all much higher isomeric yield ratios for the energies studied ^{95}Nb is not so improbable by fission of bismuth and lead(31) and according to the above discussion the ratio could be higher

Both theory(32, 33) and experiment(34) have shown, however, that for nuclei whose fission cross section is small compared to the total inelastic cross section, the fission cross section increases when the angular momentum of the target–bombarding ion system is increased, holding the total energy of the system constant If this angular momentum is connected with the rotational energy needed to obtain the deformation of the nucleus at saddlepoint, it has to be larger when going from uranium towards lead

In order to draw conclusions on these questions, one has to study more than one isomeric pair Further work is therefore in progress

The ratio ^{96}Nb/^{95}Nb This ratio was from charge distribution systematics expected to be large at low energies and to become smaller when the bombarding energy is increased That this is not the case can not be explained from present knowledge of charge distributions of fission fragments Instead it is taken to be an indication of the existence of a short lived niobium isomer with mass number 96, decaying mainly by β-decay to molybdenum The existence of such an isomer has been predicted(35) because the yield of 24 hr ^{96}Nb from thermal neutron fission of ^{235}U is lower than expected from charge distribution systematics Thus from the trend of the curves in Figs 4 and 5 it is expected that the missing isomeric state should have the lower spin of the two isomers

This ratio produced by fission of bismuth and lead shows a more expected trend, because 24 hr ^{96}Nb for all the energies studied has the highest yield, while a definite deviation is seen in Fig 4

The explanation given above is, however, somewhat unsatisfactory as careful search[36] for the lacking isomer has been unsuccessful CROALL[36] has also looked for the missing yield in thermal neutron fission of ^{235}U by studying the yield of stable ^{96}Mo Even this yield was too low Thus the field is open for new ideas.

---

(30) B L COHEN, B L FERRELL-BRYAN, D J COOMBE and M K. HULLINGS, *Phys Rev* **98,** 685 (1955)

(31) R H GOECKERMAN and I PERLMAN, *Phys Rev* **76,** 628 (1949)

(32) G A PIK-PICHAK, *Soviet Physics-JETP* **7,** 238 (1958)

(33) J R HISKES, Report UCRL-9275 (1960)

(34) J GILMORE, Report UCRL-9304 (1960)

(35) A C WAHL, *J Inorg Nucl Chem* **6,** 263 (1958)

Acknowledgements—The author is grateful to Professor T SVEDBERG for stimulating working conditions, to Professor A C PAPPAS for information on the experiments performed in Oslo, and to him and Dr B JUNG for valuable discussions

Thanks are furthermore due to Mr Å SVANHEDEN and the cyclotron staff for carrying out the numerous bombardments, and to several members of the Gustaf Werner Institute staff for various forms of assistance during the work

This work is supported by the Swedish Atomic Research Council

(36) I F CROALL Private communication (1962)

J Inorg Nucl Chem , 1963, Vol 25, pp 1213 to 1218 Pergamon Press Ltd Printed in Northern Ireland

THE YIELDS OF THE ISOMERS OF ^{81}Se AND ^{83}Se IN THE THERMAL NEUTRON FISSION OF ^{239}Pu

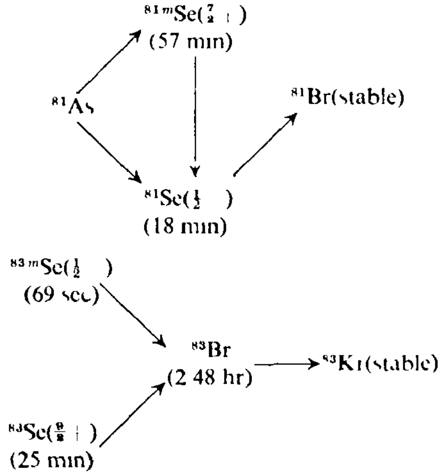
J F Croall and H H Willis
A E R E , Harwell, Didcot, Berks

(*Received* 5 *December* 1962)

Abstract—The cumulative yields of ^{81}Se, ^{81m}Se, ^{83}Se, ^{83}Br and ^{84}Br in the thermal neutron fission of ^{239}Pu have been measured radiochemically From these results and previous studies of the selenium isomer yields in ^{235}U fission, it is concluded that the ratio of the formation cross section for the high spin isomer ^{83}Se to the total formation cross section for both isomers is ≥ 0 8 Calculations based on a statistical theory of spin distributions of the nuclear level density indicate that the fragments produced in ^{239}Pu fission have a mean intrinsic angular momentum of the order of eight units

Recent measurements(1) of the cumulative yields of the isomers of ^{81}Se and ^{83}Se in the thermal neutron fission of ^{235}U and ^{233}U, and the 20 MeV-proton fission of ^{235}U have provided evidence for the favouring, in independent formation, of the high spin isomers of both nuclides in the 20 MeV proton fission of ^{235}U Reported here is the extension of these studies to the thermal neutron fission of ^{239}Pu

^{81}Se has two isomers, of which the upper level energetically, 57 min ^{81m}Se, has the higher spin (2) For ^{83}Se the ground state with half-life of 25 min is the high spin isomer and the upper level (69 sec) decays directly by β^--emission to ^{83}Kr (2) The diagram below shows the fission chains for masses 81 and 83 (2 3)


^{81m}Se($\frac{7}{2}$ +)
(57 min)
^{81}As
^{81}Br(stable)
^{81}Se($\frac{1}{2}$)
(18 min)
^{83m}Se($\frac{1}{2}$)
(69 sec)
^{83}Br
(2 48 hr)
^{83}Kr(stable)
^{83}Se($\frac{9}{2}$ +)
(25 min)

None of the yields of these selenium isomers in the thermal neutron fission of ^{239}Pu has previously been reported, and of the other yields reported in this work only that of ^{83}Br has been measured However the value of 0 08 per cent for the cumulative yield of ^{83}Br$^{(4)}$ is not consistent with the values of 0 29 per cent and 0 47 per cent reported for ^{83}Kr and ^{84}Kr respectively $^{(5\ 6)}$ This discrepency will be considered later

---

(1) I F Croall and H H Willis, *J Inorg Nucl Chem* 24, 221 (1962)

(2) K Way, R W King, C L McGinnis and R van Lieshout, U S A E C Report, TID 5300 (1955)

(3) D Strominger, J M Hollander and G T Seaborg, *Rev Mod Phys* 30, 585 (1958)

EXPERIMENTAL

The selenium and bromine yields were measured separately in two series of experiments All irradiations were made in the pneumatic tube assembly in the BEPO reactor, in a flux of the order of 1 2 10^{12} neutrons cm^{-2} sec^{-1} The lengths of the irradiations varied between 1 min and 20 min

In some early bromine runs the plutonium was irradiated in solution as plutonium (IV) nitrate,$^{(4)}$ but as consistent results could not be obtained between separate irradiations this method was abandoned In all subsequent irradiations for both bromine and selenium determinations the samples were plutonium (IV) nitrate crystals wrapped in aluminium foil The whole samples, including the aluminium foil were dissolved in dilute hydrochloric acid in the presence of bromine (in the form of bromate ion), selenium, barium and molybdenum carriers Duplicate analyses for ^{140}Ba or ^{99}Mo were carried out on small aliquots of the solution for each irradiation, the bulk of the solution being taken for the bromine or selenium analyses All radiochemical procedures employed here were the same as those adopted for the earlier studies of uranium fission $^{(1)}$

The radiochemically purified samples were mounted on tared filter paper disks using a standard filter stick $^{(1)}$ After drying and weighing they were then counted in a 2π gas-flow proportional counter

The decay of both bromine and selenium samples was followed until the counting rate was essentially the background for the counter The bromine decay curves were relatively simple, showing only 2 48 hr and 32 min components due to ^{83}Br and ^{84}Br respectively The selenium decay curve is more complex as we have 18 min ^{84}Se growing in from ^{84m}Se and ^{83}Br growing in from ^{83}Se The analysis of the decay curves was carried out on an IBM 7090 computer, using a least squares fitting programme based on the approach proposed by VON HOLDT$^{(7)}$

The counting rates of the bromine and selenium species at the end of the irradiation obtained from these analyses were corrected for self-absorption, back-scattering and counter efficiency$^{(8\ 9)}$ so as to make them strictly comparable with the ^{140}Ba and ^{99}Mo used as standards for the fission yield determinations

The cumulative fission yields of ^{140}Ba and ^{99}Mo were taken as 5 4 per cent and 6 1 per cent respectively $^{(10)}$

RESULTS

The early runs, in which the plutonium was irradiated in solution, gave erratic results for the bromine yields The cumulative yields observed were of the order of 0 06 per cent and 0 07 per cent for ^{83}Br and ^{84}Br respectively A similar experimental arrangement was used by FINKLE *et al* $^{(4)}$ to obtain a value of 0 08 per cent for the ^{83}Br yield These results are, as mentioned earlier, inconsistent with the mass spectrometrically determined yields for ^{83}Kr and ^{84}Kr. This fact, together with the spread of the present results suggested either loss of bromine or incomplete exchange between the carrier and radiogenic bromine On changing to targets consisting of solid plutonium nitrate wrapped in aluminium foil yields consistent with the ^{83}Kr and ^{84}Kr yields, and also reproducible from experiment to experiment, were observed. Eleven determinations of the bromine yields were made, the duration of the irradiations varying between 1 and 20 min and the cooling period before processing ranged from 10 min to 2 hr. The observed cumulative yields are

---

(4) B FINKLE, E J HOAGLAND, S KATCOFF and N SUGARMAN, National Nuclear Energy Series, Division IV, Vol 9, Paper 216, McGraw-Hill, New York (1953)

(5) H R FICKEL and R H TOMLINSON, *Canad J Phys* **37**, 916, (1959)

(6) K FRITZE, C C MCMULLEN and H G THODE, *Proceeding of the Second International Conference on the Peaceful uses of Atomic Energy, Geneva* 1958 Paper 187, United Nations (1958)

(7) R E VON HOLDT, Lawrence Radiation Laboratory, University of California, Livermore, California (1961)

(8) J G CUNINGHAME, M L SIZELAND and H H WILLIS, AERE-C/R 2054 (1957).

(9) J G CUNINGHAME, Private communication (1959)

(10) S KATCOFF, *Nucleonics* **18**, 201 (1960)

^{83}Br	0.303 ± 0.046 per cent
^{84}Br	0.407 ± 0.040 per cent

The limits quoted are twice the observed standard deviations, no account being taken of any errors on the assumed yields of ^{99}Mo and ^{140}Ba. No significant differences were observed between the measurements made using ^{99}Mo as the standard and those which used ^{140}Ba as the standard.

Fourteen determinations of the selenium yields were made, ten relative to ^{140}Ba and four relative to ^{99}Mo. Again, there was no observable difference between the two types of experiment. Table 1 below gives the observed cumulative yields.

TABLE 1.—CUMULATIVE YIELDS OF THE ISOMERS OF ^{81}Se AND ^{83}Se IN THE THERMAL NEUTRON FISSION OF ^{239}Pu

57 min ^{81m}Se	0.0044 ± 0.0014 per cent
18 min ^{81}Se	0.178 ± 0.025 per cent
25 min ^{83}Se	0.157 ± 0.021 per cent

DISCUSSION

Table 2 shows the ratios of the cumulative yields of the selenium isomers as determined in this work and from reference (1).

TABLE 2.—RATIOS OF THE CUMULATIVE YIELDS OF THE ISOMERS OF ^{81}Se AND ^{83}Se IN THERMAL NEUTRON FISSION

	^{233}U	^{235}U	^{239}Pu
$\frac{^{81}\text{Se}}{^{81m}\text{Se}}$	28 ± 6	23 ± 10	40 ± 15
$\frac{^{83}\text{Se}}{^{83m}\text{Se}}$	0.62 ± 0.05	0.67 ± 0.05	1.08 ± 0.13

As the cumulative yield ratio is predominantly fixed by the branching ratio of the precursors, any significant difference in the ratios is due to a difference in the proportion of the cumulative yield formed independently at the isomer pair in question. The equal charge distribution rule(11,12) predicts the following fractional chain yields for ^{83}Se in thermal neutron fission: ^{235}U 0.16, ^{233}U 0.20 and ^{239}U 0.27. No significant difference in the cumulative yield ratio for ^{83}Se between ^{235}U and ^{233}U fission is apparent. However, the 83/83*m* ratio for ^{239}Pu fission is significantly different. The increase in the proportion of the high spin isomer ^{83}Se can only be explained by the fact that independent formation of ^{83}Se and ^{83m}Se leads predominantly to the high spin isomer (^{83}Se).

---

(11) L. E. GLENDENIN, C. D. CORYELL and R. R. EDWARDS *Radio Chemical Studies. The Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN) NNES, Plutonium Project Record Div. IV, Vol. 9, Paper 52. McGraw-Hill, New York (1951).

(12) A. C. WAHL, R. L. FERGUSON, D. R. NETHAWAY, D. E. TROUTNER, K. WOLFSBERG, *Phys. Rev.* **126**, 1112 (1962).

The following equations, involving the fission yields of the ^{83}Se isomers, can be set up

$$C_U + I_U = 0.218 \qquad C_{Pu} + I_{Pu} = 0.157$$

$$C_U{}^m + I_U{}^m = 0.34 \qquad C_{Pu}{}^m + I_{Pu}{}^m = 0.146$$

$$I_U{}^m + I_U = 0.089 \qquad I_{Pu}{}^m + I_{Pu} = 0.082$$

Where I denotes the independent yields of ^{83}Se (no superscript) and ^{83m}Se (superscript m) in the thermal neutron fission of ^{239}Pu and ^{235}U as indicated by the subscripts C similarly denotes the amounts of ^{83}Se and ^{83m}Se formed by decay of their precursors

Since the precursor of ^{83}Se has a fixed branching ratio for decay we also have

$$\frac{C_U}{C_U{}^m} = \frac{C_{Pu}}{C_{Pu}{}^m}$$

Whilst this system of equations cannot be completely solved, limits on the ratios $I_U/I_U{}^m$ and $I_{Pu}/I_{Pu}{}^m$ can be obtained These are

$$0 < \frac{I_U}{I_U{}^m} < 1.6$$

and

$$\frac{I_{Pu}}{I_{Pu}{}^m} > 1.7$$

These values are consistent with values for the branching ratio for the decay of the precursors given by

$$0.52 < \frac{C_U}{C_U{}^m} < 0.91$$

The ratio $I_{Pu}/I_{Pu}{}^m$ can then be expressed, more conventionally in terms of the formation cross sections for the high spin ground state (σ_g) and the isomeric state (σ_m)

$$\frac{\sigma_g}{\sigma_g + \sigma_m} > 0.63$$

In studies of the production of isomer pairs by (n, γ) reactions it has been observed that the ratio of the cross sections for the formation of the two states is such that the isomeric state with spin closest to that of the compound nucleus is favoured$^{(13)}$ For example, in the formation of ^{83}Se by slow neutron capture in ^{82}Se (I = 0) the compound nucleus has a spin of $\frac{1}{2}$ and the observed isomer ratio $\sigma_g/(\sigma_g + \sigma_m)$ is 0.08$^{(14)}$ The compound nucleus formed by s-wave neutron capture in ^{239}Pu ($I = \frac{1}{2}$) can have spins 0 or 1, a spin distribution similar to that involved in the (n, γ) reaction on ^{82}Se, and it would therefore be expected that the low spin isomer of ^{83}Se would be favoured in fission That this is not so suggests that the formation of the fission fragments from the compound nuclear state takes place in such a manner as to introduce considerable angular momentum into the fragments This initial angular momentum distribution is then modified by neutron and γ-ray emission, but must still be characterised by a high enough root mean square angular momentum to

(13) E DER MATEOSIAN and M GOLDHABER, *Phys Rev* **108**, 766 (1957).

(14) J R ARNOLD and N SUGARMAN, *J Chem Phys* **15**, 703 (1947)

account for the favouring of the high spin isomer VANDENBOSCH and HUIZENGA(15 16) have developed a statistical method for the calculation of the isomer ratios in (n, γ) reactions where the initial angular momentum distribution in the compound nucleus is known This procedure can be reversed, and used to make an estimate of the initial angular momentum distribution in a fission fragment by comparing the observed isomer ratio with those obtained from various angular momentum distributions WARHANEK and VANDENBOSCH(17) have recently applied this method to the photofission of ^{233}U using the ^{134}Cs to ^{134m}Cs cross section ratio and to the thermal neutron fission of ^{235}U using the ^{131m}Te to ^{131}Te ratio determined by ERBEN *et al*(18) In both cases the isomer ratios were found to be consistent with an initial angular momentum distribution for the fragment characterised by a root mean square angular momentum of 8 7 or 10 depending on whether 1 or 2 neutrons are assumed to be emitted from the fragments The compound nuclei have spins of $\frac{3}{2}$, $\frac{5}{2}$ and $\frac{7}{2}$ for photofission of ^{233}U and 3 or 4 for neutron fission of ^{235}U The initial angular momentum distribution is taken to have the form

$$N(J) = (2J+1)\exp\left(-\frac{(J+1)}{2b^2}\right)$$

where $N(J)$ is the number of states with spin J and $\sqrt{2}b = \sqrt{\overline{J^2}}$, the root mean square angular momentum which characterises the distribution (17 19) The calculation of the angular momentum at various stages in the de-excitation process of neutron emission and γ-ray cascade follows the procedure given by HUIZENGA and VANDENBOSCH (16 17) It was assumed that one neutron was emitted(20) and that three gamma rays were emitted in the de-excitation process The γ-ray cascade was taken to consist entirely of dipole radiation

Table 3 shows the calculated isomer ratios for various (assumed) initial angular momentum distributions

TABLE 3 — CALCULATED $\frac{\sigma_g}{\sigma_g + \sigma_m}$ VALUES FOR THE ISOMERS OF ^{83}Se

$\sqrt{\overline{J^2}}$	$\frac{\sigma_g}{\sigma_g + \sigma_m}$
2 0	0 14
4 0	0 66
6 0	0 78
8 0	0 84

The experimental value for the isomer ratio of 0 63 corresponds to an initial distribution with $\sqrt{\overline{J^2}} > 4\ 0$ A change in the number of γ-rays involved in the

---

(15) J R HUIZENGA and R VANDENBOSCH, *Phys Rev* **120**, 1305 (1960)

(16) R VANDENBOSCH and J R HUIZENGA, *Phys Rev* **120**, 1313 (1960)

(17) R VANDENBOSCH, Argonne National Laboratory, U S A Private communication (1962)

(18) M T ERBEN, L E GLENDENIN and E P STEINBERG Argonne National Laboratory Private communication (1958)

(19) T ERICSON and V STRUTINSKI *Nucl Phys* **8**, 284 (1958)

(20) M M HOFFMAN, Los Alamos Scientific Laboratory, U S A Private communication (1962)

de-excitation from three to two or four results in a change of less than 10 per cent in the calculated isomer ratio

The initial angular momentum distribution previously estimated(17) for the thermal neutron fission of ^{235}U suggests that the high spin isomer of ^{83}Se will be favoured in this process, thus modifying the expression for $I_U/I_U{}^m$ to

$$1 < I_U/I_U{}^m < 1{\cdot}6$$

The isomer ratio estimated for ^{239}Pu fission is then changed to $\sigma_g/(\sigma_m + \sigma_g) > 0\ 8$, corresponding to $\sqrt{\bar{J}^2} \sim 8$ in the fission fragment compared with a value of 0 or 1 for the spin of the compound nucleus

Recent studies of the angular anisotropy of the gamma quanta emitted in the thermal neutron fission of ^{239}Pu have been made by HOFFMAN (20) The observed anisotropy was found to be consistent with an initial angular momentum for the fragments of six to eight units

Calculations(21 22) indicate that up to ten units of angular momentum could arise from electrostatic forces between the fragments, as a non-colinearity of the distorted fragments, just after scission has taken place, could give rise to a transverse component of coulomb repulsion between the fragments The presence of a large amount of angular momentum in the fragments is also consistent with the anisotropy of prompt neutron emission observed by RAMANNA *et al* (23)

Acknowledgements -The authors are indebted to MR G N WALTON for helpful discussions and to DR R VANDENBOSCH and DR M M HOFFMAN who made available as yet unpublished results

(21) E M GLOVER and M M HOFFMAN, *Bull Amer Phys Soc* **7,** 18 (1962)

(22) V M STRUTINSKI, *Soviet Physics JETP*, **37,** 861 (1959)

(23) R RAMANNA, R CHAUDHRY, S S KAPOOR, K MIKKE, S R S MURTHY and P N RAMA RAO, *Nucl Phys* **25,** 136 (1961)

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 1219 to 1223. Pergamon Press Ltd. Printed in Northern Ireland

CHEMICAL SHIFTS OF THE METHYL DERIVATIVES OF THE REPRESENTATIVE ELEMENTS

C. R. McCoy and A. L. Allred
Department of Chemistry, Northwestern University, Evanston, Illinois

(*Received* 1 *April* 1963)

Abstract—The trends of the proton chemical shifts exhibited by the simple methyl compounds of the elements in the zinc, carbon, nitrogen, oxygen and fluorine groups are summarized and discussed in terms of the polarities of the carbon–metal bonds and other factors. The chemical shifts of the methyl derivatives of zinc, cadmium and mercury are consistent with the relative electronegativities increasing monotonically with period number and having the values 1.65, 1.69 and 2.00, respectively, for these elements in divalent states.

Numerous reports have dealt with the nuclear magnetic resonance (N.M.R.) spectra of alkyl groups bonded to various elements and functional groups. The complexity of the factors which determine the chemical shifts is widely recognized, and, at present, there are no general methods for predicting the relative chemical shifts of methyl and other alkyl groups in very different types of environments. However, the proton chemical shifts of the methyl halides at infinite dilution in an inert, magnetically isotropic solvent are a linear function of electronegativity of the halogens,(1, 2) and comparable variations are observed for the proton resonance of the tetramethyl compounds of the carbon group(3, 4) and the trimethyl compounds of the nitrogen group.(5) The order of increasing chemical shifts of ^{13}C in the tetramethyl compounds of the carbon group does not parallel the order for ^{1}H.(6)

To determine if a general trend exists for the chemical shifts of methyl derivatives of the representative elements, additional chemical shift data have been collected and some existing data have been treated to obtain chemical shifts for methyl compounds in a common solvent.

EXPERIMENTAL

Preparation of compounds

Dimethylzinc, dimethylcadmium and dimethylmercury were prepared and analysed by previously described procedures.(7, 8, 9) Dimethylsulphide (Eastman) and carbon tetrachloride (Eastman) were used without additional purification. Tetramethylsilane (Anderson Chemical Company) was redistilled after shaking with sulphuric acid.

(1) A. L. Allred and E. G. Rochow, *J. Amer. Chem. Soc.* **79**, 5361 (1957).
(2) B. P. Dailey and J. N. Shoolery, *J. Amer. Chem. Soc.* **77**, 3977 (1955).
(3) A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, **5**, 269 (1958).
(4) A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, **20**, 167 (1961).
(5) A. L. Allred and A. L. Hensley, Jr., *J. Inorg. Nucl. Chem.* **17**, 43 (1961).
(6) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.* **35**, 722 (1961).
(7) H. Gilman and R. E. Brown, *J. Amer. Chem. Soc.* **52**, 3314 (1930).
(8) H. Gilman and J. F. Nelson, *Rec. Trav. Chim.* **55**, 518 (1936).
(9) C. R. McCoy and A. L. Allred, *J. Amer. Chem. Soc.* **84**, 912 (1962).

N.M.R. measurements

N.M.R. spectra were observed at 25 ± 1.5°C with a Varian Associates, Inc., high-resolution spectrometer operating at 60 Mc/s for dimethylsulphide and at 40 Mc/s for dimethylzinc, dimethylcadmium and dimethylmercury. Each compound was investigated at five or six concentrations ranging from 2.5 to 100 per cent. The 5 mm o.d. Pyrex sample tube contained a sealed glass capillary filled with benzene (external reference).

The chemical shifts were measured by the side-band technique and are reported in parts per million.

RESULTS

The chemical shifts of pure dimethylzinc, dimethylcadmium, dimethylmercury, and dimethylsulphide are 6.84, 6.25, 5.46 and 4.63 p.p.m., respectively, with respect to the external reference, benzene, which exhibits resonance at a lower applied field. The chemical shifts extrapolated to infinite dilution for these compounds and the solvents are tabulated in Table 1. In all cases, the variation of chemical shift with concentration is linear.

TABLE 1. CHEMICAL SHIFTS OF METHYL COMPOUNDS

	δ* (p.p.m.)	Solvent	External reference	δ′† Calc. (p.p.m.)	Electronegativity(10)
F	0.53(1)	CCl_4	H_2O	2.26	3.98
Cl	1.74(1)	CCl_4	H_2O	3.47	3.16
Br	2.10(1)	CCl_4	H_2O	3.83	2.96
I	2.60(1)	CCl_4	H_2O	4.33	2.66
O	1.55(1)	CCl_4	H_2O	3.28	3.44
S	4.41	CCl_4	C_6H_6	4.41	2.58
N	3.18(5)	$C(CH_3)_4$	H_2O	4.30	3.04
P	4.35(5)	$C(CH_3)_4$	H_2O	5.47	2.19
As	4.39(5)	$C(CH_3)_4$	H_2O	5.51	2.18
Sb	4.53(5)	$C(CH_3)_4$	H_2O	5.65	2.05
Bi	4.19(5)	$C(CH_3)_4$	H_2O	5.31	2.02
C	3.85(3)	CCl_4	H_2O	5.58	2.55
Si	4.74(3)	CCl_4	H_2O	6.47	1.90
Ge	4.62(3)	CCl_4	H_2O	6.35	2.01
Sn	4.70(3)	CCl_4	H_2O	6.43	1.96
Pb	4.04(3)	CCl_4	H_2O	5.77	2.33
Zn	7.41	$Si(CH_3)_4$	C_6H_6	7.01	1.65
Cd	7.32	$Si(CH_3)_4$	C_6H_6	6.92	1.69
Hg	6.61	$Si(CH_3)_4$	C_6H_6	6.21	2.00

* Extrapolated to infinite dilution.

† Infinite dilution in carbon tetrachloride with benzene as the external reference. All resonances occur at higher applied fields than that required for benzene.

Also tabulated in Table 1 are the chemical shifts for fifteen other methyl derivatives at infinite dilution in either neopentane or carbon tetrachloride.

In column 5 of Table 1 are the calculated or observed chemical shifts with respect to the external reference, benzene, for the methyl derivatives at infinite dilution in the common solvent, carbon tetrachloride. Some of the methyl compounds of the Group II and Group V elements react rapidly with carbon tetrachloride and could not be observed directly in that solvent. For the compounds of Group V, it was assumed that the resonance positions with respect to an external reference decrease by the same amount (average 0.61 p.p.m.[9]) in going from infinite dilution in neopentane to infinite dilution in carbon tetrachloride as the proton resonances of methyl halides decrease with an identical change in solvents. Also, the calculated values of δ' for dimethylzinc, dimethylcadmium and dimethylmercury are based on the observation that the chemical shift (external reference) of tetramethylsilane in pure tetramethylsilane is greater than that of tetramethylsilane (using the same external reference) at infinite dilution in carbon tetrachloride by 0.40 p.p.m.[1]

The chemical shifts, relative to methane gas, of twelve gaseous methyl compounds, observed by SPIESECKE and SCHNEIDER,[6] can be compared with calculated and observed values in Table 1. By the addition of 6.30 p.p.m. to these chemical shift values for gases, the corresponding chemical shifts in column 5 of Table 1 are obtained to within $\pm$0.15 p.p.m. with an average deviation of 0.07 p.p.m. Thus solvent effects are fairly constant.

DISCUSSION

Chemical shifts. Fig. 1 is a plot of electronegativity[10] difference, $\chi_Y-\chi_C$, for the components of the C—Y bond vs. the corresponding chemical shifts, δ' in column 5.

Several trends are apparent in Fig. 1.

(1) Considering all of the data, one finds a rough linear correlation of $\chi_Y-\chi_C$ with δ'.

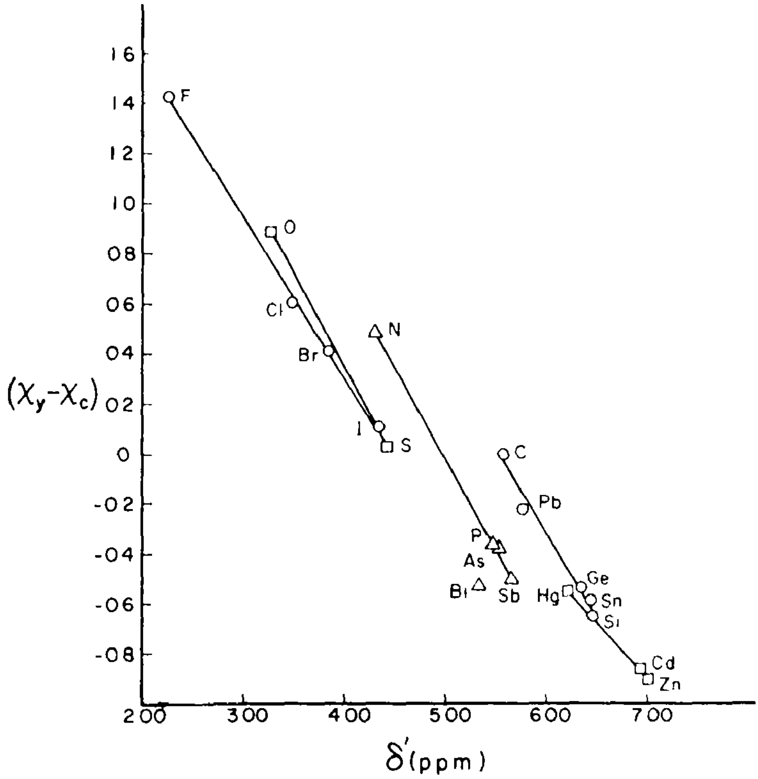


FIG. 1.—Plot the difference of electronegativity, $\chi_Y-\chi_C$ for the carbon-representative element bond vs. the proton chemical shift of the methyl group.

---

[10] A. L. ALLRED, *J. Inorg. Nucl. Chem.* **17**, 215 (1961).

(2) For the individual groups of elements, in the periodic system, there is little scatter of points from straight lines.
(3) The lines are approximately parallel.
(4) The points for the compounds which are formed by the elements of Groups II and IV and which do not contain "lone pairs" of electrons could be fitted approximately by a single line. Displaced toward lower fields from the Group II–IV line are lines for Group V, Group VI, and Group VII, respectively, corresponding to the order of increasing number of "lone pairs": zero, one, two, and three. *The increase in chemical shift upon replacing* Y with Y—C is reminiscent of the up-field shift upon replacing C—H by C–C in a large number of alkyl derivatives.(11, 12)
(5) In the plot of $\chi_X - \chi_C$, obtained by the common thermochemical method with recent data, as a function of δ', the points for the sixth period elements, mercury, lead and bismuth tend to be displaced slightly to lower fields, possibly due to a paramagnetic contribution.(13)

Table 2. Reported values of electronegativities of the elements of Group II-B

	Zn	Cd	Hg
Thermochemical data			
Reference 10	1.65	1.69	2.00
Pauling(15)	1.6	1.7	1.9
Work function(16)	1.5	1.6	1.8
Electrostatics			
Z_{eff}/r(17)	1.21	1.13	-
Z_{eff}/r^2(18)	1.66	1.46	- -
Stability ratio(19)	1.86	1.73	1.92
Force constant(16, 20)	*	*	1.8

* Not reported for divalent compounds.

The trimethyl compounds of Group III-B elements have not been included here due to varying tendencies toward dimerization. However, the internal chemical shifts, ($\delta_{CH_3}-\delta_{CH_2}$), of the ethyl derivatives have been correlated with the electronegativities of the Group III elements.(11)

Electronegativities of zinc, cadmium and mercury. Various methods for estimating the electronegativities of the elements of Groups IV and V have been discussed elsewhere.(3,4,5) For the zinc, cadmium and mercury group, values of electronegativity from various scales are assembled in Table 2.

(11) A. A. Bothner-By and C. Naar-Colin, *Ann. N.Y. Acad. Sci.*, **70**, 833 (1958).
(12) J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.* **34**, 1099 (1961) and references therein.
(13) N. F. Ramsey, *Phys. Rev.* **86**, 243 (1952).
(14) S. Brownstein, B. C. Smith, G. Ehrlich and A. W. Laubengayer, *J. Amer. Chem. Soc.* **81**, 3826 (1959).
(15) L. Pauling, *Nature of the Chemical Bond* p. 93. Cornell, Ithaca (1960).
(16) W. Gordy and W. J. O. Thomas, *J. Chem. Phys.* **24**, 439 (1956).
(17) W. Gordy, *Phys. Rev.* **69**, 604 (1946).
(18) A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.* **5**, 264 (1958).
(19) R. T. Sanderson, *Chemical Periodicity* p. 34. Reinhold, New York (1960).
(20) W. Gordy, *J. Chem. Phys.* **14**, 305 (1946).

There is considerable divergence in both order and magnitude of the values in Table 2. The scales from electrostatic potential, electrostatic force and "stability ratios" are based on crude models and, in this case, the electronegativities from thermochemical data and from work functions may be more reliable. For each of these Group II elements, the three computations, based on ΔH_f° for dichlorides, dibromides, and diiodides, agreed well with each other.[10] The increasing order of electronegativities, $\chi_{Zn} < \chi_{Cd} < \chi_{Hg}$, from thermochemical data is consistent with the decreasing order of chemical shifts, $\delta_{(CH_3)_2Zn} = 7.01$, $\delta_{(CH_3)_2Cd} = 6.92$ and $\delta_{(CH_3)_2Hg} = 6.21$ p.p.m. of the methyl derivatives of these divalent elements. The electronegativities from work functions indicate that the order of electron-attracting ability of the uncombined metals is also $\chi_{Zn} < \chi_{Cd} < \chi_{Hg}$.

Acknowledgements—We wish to express appreciation to the Research Corporation and to the Esso Education Foundation for generous support of this research.

J. Inorg. Nucl. Chem. 1963. Vol. 25, pp. 1225 to 1238. Pergamon Press Ltd. Printed in Northern Ireland

THE STABILITIES OF THE ALKALINE EARTH CHELATES OF SOME POLYAMINOPOLYCARBOXYLIC ACIDS

J. H. GRIMES, A. J. HUGGARD and S. P. WILFORD
Atomic Weapons Research Establishment, Aldermaston

(*Received* 20 *December* 1962; *in revised form* 27 *March* 1963)

Abstract—Interactions of the alkaline earth metals with some polyaminopolycarboxylic acids have been investigated by the potentiometric titration method for aqueous solutions of ionic strength approximately 0.1 at 30°. Metal chelate formation constants have been calculated, and the effects of ligand structure on chelate stability are discussed.

THE alkaline earth metals are well known to form strong complexes with compounds containing iminodiacetic acid groups. The stabilities of these complexes can be correlated with a number of ionic properties,[1] and for calcium, strontium and barium, stability constants with the same ligand are invariably found to be in the order $K_{CaL} > K_{SrL} > K_{BaL}$ (i.e. in the inverse order to that of the ionic radii). For calcium and magnesium, the order predicted from ionic properties ($K_{MgL} > K_{CaL}$) is frequently reversed, particularly with the polyaminopolycarboxylic acids. This is generally attributed to the overcrowding of donor groups round the metal ion, resulting in mutual repulsion. In the particular case of the magnesium ion and EDTA, HUGHES and MARTELL[2] have suggested that overcrowding prevents some of the donor groups from displacing water molecules from the solvent sheath of the ion, so that fewer are displaced into solution than are from the calcium ion. However, calorimetric data[3] indicate that the enthalpy change, unlike the entropy change, is higher for calcium, from which it may be deduced that the spatial configuration of EDTA is such that the calcium ion co-ordinates in all six positions with less strain. This deduction is supported by infra-red spectroscopic data on the solid alkaline earth EDTA chelates.[4]

A large number of iminodiacetic acid derivatives is now known, and it is therefore possible to study the influence of electronic and steric variation on the order and degree of complex stability with a closely related group of metals. A detailed analysis of this nature has been made by SCHWARZENBACH *et al.*,[5] who studied the effect of various functional groups as partners to a single iminodiacetic acid residue. The results were interpreted using the correlation between acid dissociation constant and metal stability constant—this relationship between ligand basicity and chelate stability has been well discussed in the literature.

In this paper this method of interpretation is used in the study of some other ligands.

---

[1] A. E. MARTELL and M. CALVIN, *Chemistry of the chelate compounds*, Prentice-Hall, Englewood Cliffs (1956).

[2] V. L. HUGHES and A. E. MARTELL, *J. Amer. Chem. Soc.* **78**, 1319 (1956).

[3] R. A. CARE and L. A. K. STAVELEY, *J. Chem. Soc.* 4571 (1956).

[4] D. T. SAWYER and P. J. PAULSEN, *J. Amer. Chem. Soc.* **80**, 1597 (1958).

[5] G. SCHWARZENBACH, G. ANDEREGG, W. SCHNEIDER and H. SENN, *Helv. Chim. Acta*, **38**, 1147 (1955).

EXPERIMENTAL

Materials

The following ligands were studied:

1,2-diaminopropane-NNN′N′-tetra-acetic acid* (C-Me-EDTA) H_4L
ethylenediamine-NN′-diacetic acid-NN′-di-2-propionic acid* (EDDADP) H_4L
NN′-bis(aminoethyl)ethylenediamine-NN′N′N″N‴N‴-hexa-acetic acid* (TTHA) H_6L
2-hydroxy-1,3-diaminopropane-NNN′N′-tetra-acetic acid† (HPDTA) H_4L
o-phenylenediamine-NNN′N′-tetra-acetic acid (*o*-PDTA) H_4L
1,3,5-triaminocyclohexane-NNN′N′N″N″-hexa-acetic acid (CTHA) H_6L

Analyses of the commercially obtained ligands, after water washing and drying to constant elemental analysis, showed that they could be used without further purification (in some cases hydrates were obtained). These analyses were C-Me-EDTA (Found C, 43.2, H, 6.2, N, 9.15 Calc for $C_{11}H_{18}N_2O_8$ C, 43.1, H, 5.9, N, 9.15%) EDDADP (Found C, 42.6, H, 6.9, N, 8.4 Calc for $C_{12}H_{20}N_2O_8 \cdot H_2O$ C, 42.6, H, 6.6, N, 8.3%) TTHA (Found C, 43.6, H, 6.1, N, 11.2 Calc for $C_{18}H_{30}N_4O_{12}$ C, 43.7, H, 6.1, N, 11.3%) HPDTA (Found C, 35.1, H, 6.1, N, 7.7 Calc for $C_{11}H_{18}N_2O_9 \cdot 3H_2O$ C, 35.1, H, 6.4, N, 7.4%)

o-phenylenediamine-NNN′N′-tetra-acetic acid (*o*-PDTA) was prepared by the method of OTOZAI and KATO⁽⁶⁾ (Found C, 49.5, H, 4.9, N, 8.2, equivalent weight 86.1 Calculated for $C_{14}H_{16}N_2O_8$ C, 49.4, H, 4.7, N, 8.2%, equivalent weight 85.0). Solutions of *o*-PDTA deteriorate with time, this effect being enhanced by ultra-violet light, and maximum stability was obtained by keeping the solid in a dry state in the absence of light.

1,3,5-triaminocyclohexane-NNN′N′N″N″-hexa-acetic acid (CTHA) was prepared using phloroglucinol as the starting material.

Phloroglucinol trioxime was prepared from phloroglucinol (A.R. grade, Messrs. B.D.H. Ltd.) by a procedure based on Baeyer's method.⁽⁷⁾ Phloroglucinol dihydrate (81 g, 0.5 mole) was added to an ice-cold mixture of hydroxylamine hydrochloride (121.5 g, 1.75 moles) and potassium carbonate (121.5 g, 0.88 mole) in 3.5 l. of water. The reaction mixture was placed in a darkened polythene container and stored in a refrigerator (5°). After 12 hr the mixture was filtered to remove undissolved materials, necessary precautions being taken to exclude light. The filtrate was replaced in the darkened container and left in the refrigerator for seven days. The mixture was then filtered and the precipitate obtained leached twice with boiling ethanol. The crude phloroglucinol trioxime, so obtained, was purified by recrystallization from methanol, giving the pure trioxime in 65 per cent yield, m.p. 155°(d) (Found C, 42.4, H, 5.5, N, 23.9 Calc for $C_6H_9N_3O_3$ C, 42.1, H, 5.3, N, 24.6%)

Phloroglucinol trioxime was reduced to cyclohexane 1,3,5-triamine (ccc) by the method of LIONS and MARTIN.⁽⁸⁾ The triamine was obtained in 46 per cent yield as a clear liquid, b.p. 103°/2 mm, and was characterized as the tri-hydrochloride monohydrate, m.p. 320°. LIONS and MARTIN cite 110°/2.7 mm and 320° respectively.

CTHA was prepared by adding a solution of potassium chloroacetate (Prepared using "Analar" reagents 12.5 g in the minimum amount of water.) to a solution of cyclohexane-1,3,5-triamine (2.6 g in the minimum amount of water). A yellow colour developed in the mixture. Over a period of 3 hr a concentrated aqueous solution of potassium hydroxide (11 g) was added, whilst the mixture was stirred and heated at 85°. The temperature was maintained for a further seventy hours and then, after cooling, concentrated hydrochloric acid was added until the pH was about 2. The mixture (20 ml) was poured into methanol (300 ml) and left standing for about eighteen hours at 0°. The precipitate which was formed was collected by filtration and twice purified by precipitation from water/methanol to give a white solid, m.p. 200°, which elemental analysis showed to be *cyclohexane*-1,3,5-*triamine-NNN′N′N″N″-hexa-acetic acid tri-hydrate with 0.05 molar proportions of ionizable* hydrogen replaced by potassium (Found C, 40 15, H, 5 7, N, 7 55, K (as ash), 2 0, Cl, 0 1, molecular weight 540 $C_{18}H_{26\,7}N_3O_{12}K_{0\,3}3H_2O$ requires C, 39 8, H, 6 1, N, 7 7, K, 2 2%, molecular weight 543) A silver nitrate test indicated that chloride ion was absent Titration confirmed partial neutralization by 0 05 molar proportions of base

---

* The Geigy Company Ltd.

† Aldrich Chemical Co., Inc.

⁽⁶⁾ K. OTOZAI and I. KATO, *Japan Analyst* **8**, 259 (1959).

⁽⁷⁾ A. BAEYER, *Ber. Dtsch. Chem. Ges.* **19**, 159 (1886).

⁽⁸⁾ F. LIONS and K. V. MARTIN, *J. Amer. Chem. Soc.* **79**, 1572 (1957).

The concentrations of the ligand solutions used (~ 1 × 10^{-3} M) were determined by titration with a standard zinc solution using a metallochromic indicator

Standard metal solutions and the carbonate free potassium hydroxide solution, used for titrations, were specially prepared by Messrs B D H Ltd

In accordance with much published work,[9] all titrations were carried out in the presence of a constant concentration of inert salt (0 1 M potassium chloride) Background acid (1 10^{-3} M perchloric acid) was present in those titrations where the stability constants were to be calculated after IRVING [10] "Analar" water (Messrs B D H Ltd) was used in the preparation of all solutions

Apparatus

Measurement of pH was made with an Electronic Instruments Ltd direct reading pH meter (Model 23A) using a glass electrode (E I L GHS23) and a reference electrode (E I L RJ23 Calomel) The instrument was standardized before each titration with solutions prepared from Burroughs Wellcome buffer tablets (these conform to N B S definition of pH) Measurements of pH were accurate to ± 0 02 pH units Titrations were carried out at 30 0 0 2 in a double-walled glass cell of total capacity 250 ml Water from a thermostat circulated through the outer jacket An "agla" micrometer syringe was used for alkali addition, a very fine polythene capillary being employed to prevent diffusion of alkali into the solution

Titration procedure

The appropriate solution (200 ml in all cases) was pipetted into the titration cell, the electrodes and stirrer placed in position, and oxygen-free nitrogen, presaturated with water vapour by passing through water at 30 bubbled through the solution When temperature equilibrium had been reached, the titration was carried out, time being allowed for equilibration after each addition of alkali curves were plotted of pH versus ml of alkali added For a particular ligand the following titration curves were plotted, according to the method of calculation employed (IRVING and ROSSOTTI[10] or SCHWARZENBACH and ACKERMANN[11])

Irving (a) Perchloric acid (b) perchloric acid + ligand (c) perchloric acid + ligand metal, equal concentrations of ligand and metal

Schwarzenbach (a) ligand (b) ligand metal ten times excess of metal (c) ligand metal, equal concentration of metal

CALCULATIONS AND RESULTS

It should be noted that all the values reported here are stoicheiometric concentration constants, valid only for the conditions of solvent and ionic background under which they were obtained

Constants for C-Me-EDTA, HPDTA *and* EDDADP

The acid dissociation constants, and chelate stability constants with the alkaline earth metals, of C-Me-EDTA, HPDTA and EDDADP were calculated by the method of IRVING and ROSSOTTI [10, 12] A special feature of this method is that the formation curve of a system of metal–ligand complexes can be calculated directly from pH meter readings during a titration, without knowledge of the hydrogen ion concentration or activity This method of calculation makes no allowance for the formation of protonated and/or binuclear complexes, but Schwarzenbach and Ackermann(13) have shown that for EDTA an analogous compound—the protonated complex is an unstable intermediate never present to more than a few per cent, and that the binuclear complex is not formed under normal conditions Also the presence of these additional complexes leads to unusual formation function curves which were not obtained for the above compounds The results are given in Table 1, together with other authors' data relevant to the discussion

---

[9] J BJERRUM, G SCHWARZENBACH and L G SILLEN *Stability Constants Part* 1 *Organic Ligands* Chem Soc , London (1956)

[10] H M IRVING and H S ROSSOTTI, *J Chem Soc* 2904 (1954)

[11] G SCHWARZENBACH and H ACKERMANN, *Helv Chim Acta* **31**, 1029 (1948)

[12] H IRVING and H S ROSSOTTI, *J Chem Soc* 3397 (1953)

Table 1

Compound	Acid dissociation constants				Chelate stability constants			
	pK_1	pK_2	pK_3	pK_4	$\log K_{Mg}$	$\log K_{Ca}$	$\log K_{Sr}$	$\log K_{Ba}$
(1) C-Me-EDTA	2 60	3 03	6 20	10 84	10 29	11 47	9 61	8 48
(2) HPDTA	~2	3 36	6 85	9 70	5 3	6 52	5 10	4 65
(3) EDDADP	2 29	2 91	6 82	10 60	9 41	10 74	8 68	6 86
(4) EDTA	2 4	2 86	6 22	10 25	—	10 59	8 80	—
(5) C-Me-EDTA(11)				—	8 8	10 4	10 7	8 1
(6) HPDTA(14)	—	—	—	—	5 3	6 0	5 1	4 7
(7) TMDTA(11)	2 0	2 67	7 91	10 27	6 02	7 12	5 18	4 24

(1), (2), (3), (4)—present authors 30°, in 0 1 M KCl
(5), (6)—ref 14, no experimental details given
(7)—ref 11, trimethylenediamine-NNN′N′-tetra-acetic acid, 20 , in 0 1 M KCl

Constants for TTHA, CTHA *and o*-PDTA

The appropriate constants for TTHA, CTHA and *o*-PDTA were calculated by an extension of the method of Schwarzenbach and Ackermann(11), the previous method(10 12) was not used (except for *o*-PDTA *v i*) because examination of the titration curves suggested that protonated metal chelates are stable species and this was confirmed by its application to TTHA, which resulted in abnormal formation function curves The method used involved the conversion of pH meter readings into hydrogen ion concentrations This problem has been considered by Bates(15) and Feldman (16) Bates, in discussing the interpretation of pH values as measured on the NBS scale, considers that a measured pH may be expected to approach an experimental $-\log f_{H^+} m_{H^+}$ provided that the test solution has an ionic strength within the same range as that of the standard buffer solution, namely between 0 01 and 0 1 Under these conditions [H$^+$] can be calculated with an error of not greater than ±0 01 pH units, provided that f_{H^+} is calculated using the same expression as was used for the assignment of the pH values of the standard buffer solutions. This expression is,

---

(13) G Schwarzenbach and H Ackermann, *Helv Chim Acta*, **30**, 1798 (1947)

(14) R L Smith, *The sequestration of metals*, Chap 5 Chapman and Hall, London (1959)

(15) R G Bates, *Electrometric pH determination*, Chap 4 Wiley, New York (1954)

(16) I Feldman, *Analyt Chem* **28**, 1859 (1956)

$$-\log f_i = \frac{AZ_i^2\sqrt{\mu}}{1 + Ba_i\sqrt{\mu}} \tag{1}$$

a_i, A and B being assigned the values as used by the NBS. As the errors introduced by this are less than the experimental error, calibration against a hydrogen electrode was considered unnecessary.

Thus, from Equation (1) the following relationship was used to obtain hydrogen ion concentrations

$$-\log_{10}[H^+] = \text{pH reading} - 0.11 \tag{2}$$

Equation (2) is calculated for an ionic strength of 0.1. Although the ionic strength varied slightly according to the concentrations of ligand and metal present, the effect of this can readily be shown to be negligible using Equation (1).

Dealing first with CTHA and TTHA, the acid dissociation constants of these compounds were calculated essentially by the method of SCHWARZENBACH *et al*.$^{(17)}$ except that an algebraic method of solution was used instead of a graphical one (acid dissociation constants are defined as follows: for an acid H_nL, $K_i = [H][H_{n-i}L]/[H_{n-i+1}L]$ and $pK_i = -\log_{10} K_i$). The value of the ionization constant for water, K_w^c (i.e. $C_{H^+}C_{OH^-}$), used in these calculations was 2.35×10^{-14}, this value being obtained from published data.$^{(18)}$

Examination of the potentiometric titration curves for these compounds, alone and in the presence of metal ions, indicates that chelation commences when the species H_3L^{3-} is present. Thus, in titrations containing excess metal ion, the possible chelate species are MH_2L^{2-}, MHL^{3-}, ML^{4-} and M_2L^{2-} their respective stability constants being

$$K_{MH_2L} = \frac{[MH_2L]}{[M][H_2L]} \quad (3) \qquad K_{MHL} = \frac{[MHL]}{[M][HL]} \quad (4)$$

$$K_{ML} = \frac{[ML]}{[M][L]} \quad (5) \qquad K_{M_2L} = \frac{[M_2L]}{[M][ML]} \quad (6)$$

The relative importance of these species can only be assessed from their respective stability constants, deductions from the shapes of the titration curves being misleading.

Using the approach of SCHWARZENBACH and ACKERMAN,$^{(11)}$ the titration curves when excess metal ion is present (Fig. 1 TTHA, Fig. 2 CTHA) may be defined in terms of the first three acid dissociation constants K_1, K_2 and K_3, and three new composite "acid" dissociation constants

$$K_4' = \frac{[H]([H_2L] + [MH_2L])}{[H_3L]} \tag{7}$$

$$K_5' = \frac{[H]([HL] + [MHL])}{([H_2L] + [MH_2L])} \tag{8}$$

$$K_6' = \frac{[H]([L] + [ML] + [M_2L])}{([HL] + [MHL])} \tag{9}$$

---

(17) G. SCHWARZENBACH, A. WILLI and R. O. BACH *Helv. Chim. Acta* 30, 1303 (1947).

(18) H. S. HARNED and B. B. OWEN *The physical chemistry of electrolytic solutions* Chap. 15. Reinhold, New York (1958).

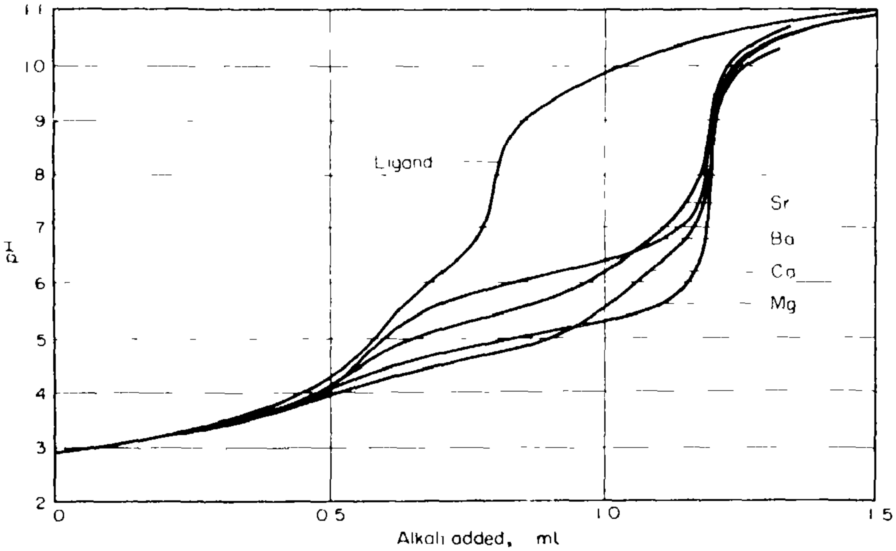


FIG 1 Titration of TTHA metal
Titration of TTHA in the absence and in the presence of ten times excess of alkaline earth ions

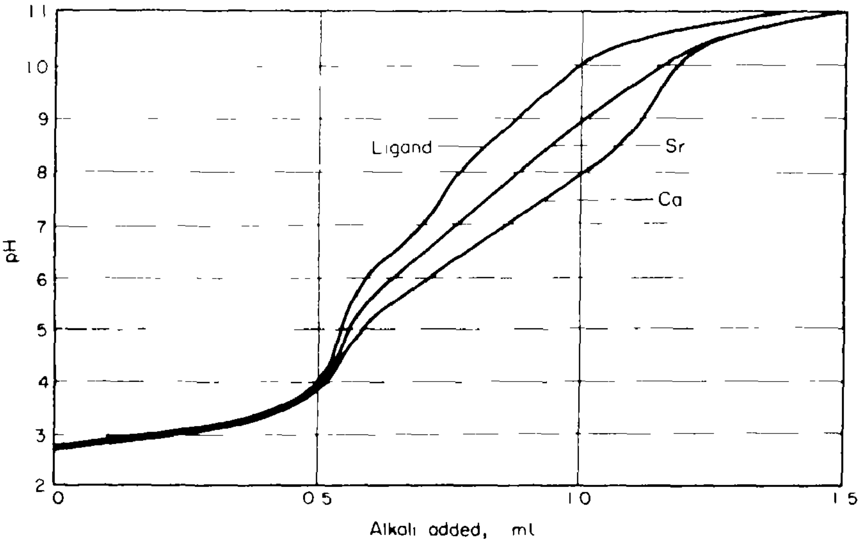


FIG 2—Titration of CTHA—metal
Titration of CTHA in the absence and in the presence of ten times excess of calcium and of strontium ions

The constants K_4', K_5' and K_6' are obtained by the usual algebraic process, by treating the excess metal curve as a simple dissociation curve. Using an essentially similar algebraic treatment to that of the above authors, the following equations may be obtained:

$$K_{MH_2L} = \frac{K_4'}{K_4 Mt} - \frac{1}{Mt} \tag{10}$$

$$K_{MHL} = \frac{K_5'(1 + \mathrm{Mt}\,K_{MH_2L})}{K_5 Mt} - \frac{1}{Mt} \tag{11a}$$

$$= \frac{K_4'K_5'}{K_4K_5\,Mt} - \frac{1}{Mt} \tag{11b}$$

and

$$K_{ML} + K_{ML}\,K_{M_2L}\,Mt = \frac{K_6'(1 + Mt\,K_{MHL})}{K_6 Mt} - \frac{1}{Mt} \tag{12a}$$

$$= \frac{K_4'\,K_5'\,K_6'}{K_4\,K_5\,K_6\,Mt} - \frac{1}{Mt} \tag{12b}$$

[N.B. Mt = concentration of metal ion, which is effectively constant as it is present in large excess.]

Thus, values for K_{MH_2L} and K_{MHL} can be calculated and further, if it is assumed that the concentration of the binuclear complex is negligible, a value for K_{ML} can be obtained.

In the titrations of equimolar mixtures of ligand and metal ion (Fig. 3 TTHA, Fig. 4 CTHA) the presence of binuclear complexes may be disregarded. Since values for K_{MH_2L} and K_{MHL} are known, data from these titrations may be used to calculate values for K_{ML} which are not dependent on the assumption made above. The method of calculation used was the same as that outlined by SCHWARZENBACH and ACKERMAN, except in the cases of calcium and magnesium with TTHA. In these cases the titration curves have large inflexions at $a = 5$*, indicating that the further release of a proton in the region $a = 5$ to $a = 6$ may be treated as a simple acid dissociation i.e.

$$\mathrm{MHL} \xrightarrow{K^{H}_{MHL}} \mathrm{ML} + \mathrm{H}$$

The constant K^{H}_{MHL}, found by the standard method, is related to K_{ML} by

$$K_{ML} = \frac{K^{H}_{MHL}\,K_{MHL}}{K_6} \tag{13}$$

Substitution of the true value for K_{ML} into (12a) or (12b) allows the calculation of K_{M_2L}. The results for TTHA and CTHA are given in Table 2.

The acid dissociation constants and chelate stability constants of *o*-PDTA were obtained by two independent methods: SCHWARZENBACH's(11, 17) method of

---

* a = no. of moles of alkali added per mole of ligand.

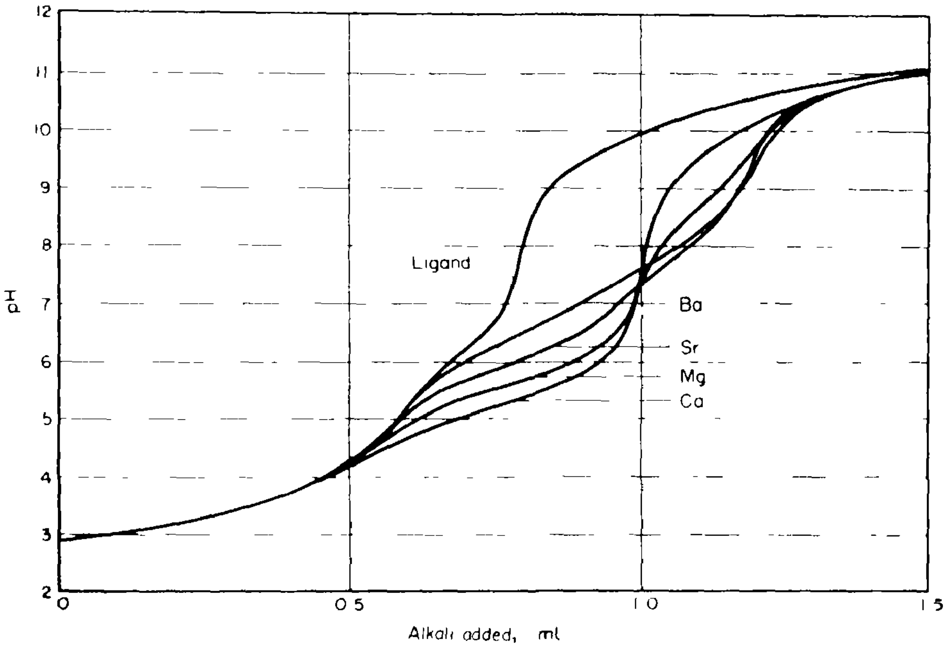


FIG 3 — Titration of TTHA—metal
Titration of TTHA in the absence and in the presence of equimolar alkaline earth ions

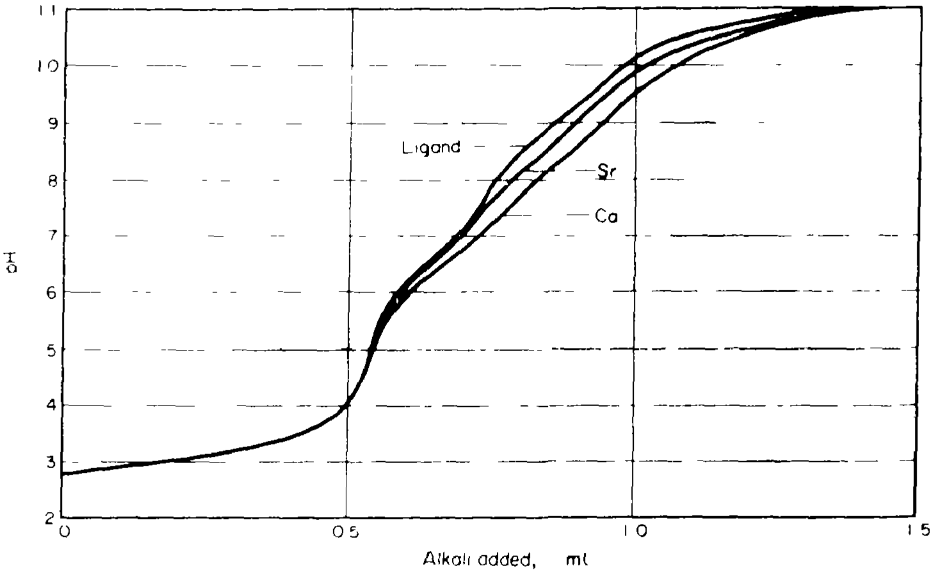


FIG 4 —Titration of CTHA – metal
Titration of CTHA in the absence and in the presence of equimolar calcium and strontium ions

calculation was applied to the titration curves in Figs 5 and 6 (excess and equimolar metal respectively), and IRVING's[10 12] method was applied to the titration curves in Fig 7

Dealing first with SCHWARZENBACH's[11,17] method, the calculation of acid dissociation constants, using an algebraic method of solution, was subject in this particular case to some inaccuracy due to arithmetical difficulties Values of pK's so obtained are therefore given to 0 1 log unit only Since chelation begins before the species H_2L is present, the method used for the calculation of chelate stability constants from the excess metal curves was modified to include four "composite" dissociation constants, defined analogously to those shown previously The flatness of the metal curves introduces considerable arithmetical uncertainties into the calculations, and, in some cases, values of individual "composite" constants and products thereof were either

TABLE 2

Metal	Acid dissociation constants						Chelate stability constants			
	pK_1	pK_2	pK_3	pK_4	pK_5	pK_6	$\log K_{MH_2L}$	$\log K_{MHL}$	$\log K_{ML}$	$\log K_{M_2L}$
							TTHA			
H	2 46	2 52	4 00	5 98	9 35	10 33				
Mg							1 9	7 39	8 47	5 94
Ca							2 4	8 07	10 06	4 10
Sr							1 6	6 71	9 26	3 44
Ba							1 7	5 55	8 22	3 41
							CTHA			
	pK_1 ¦ pK_2 ¦ pK_3									
H		6 6		6 3	8 5	10 6				
Ca							2 9	4 7	5 5	3 6
Sr							2 3	3 5	4 5	2 1
							o-PDTA			
							Calculated after SCHWARZENBACH[11 17]			
H	2 9	3 7	4 8	6 7	—	—				
Mg							2 6	*	7 1	—
Ca							*	*	~9	—
Sr							1 3	3 0	6 2	—
Ba							1 6	2 3	4 8	—
							Calculated after IRVING and ROSSOTTI[10 12]			
H	2 94	3 83	5 01	6 82	—	—				
Mg							—	—	7 3	—
Ca							—	—	8 1	—
Sr							—	—	6 4	—
Ba							—		4 8	—

* These constants could not be calculated

doubtful or unobtainable Consistent results were obtained for K_{ML} except in the case of calcium where values varied widely With strontium and barium, where protonated chelate constants were obtained, it was possible to calculate K_{ML} from the equimolar metal curves and comparison of the results obtained with those from the excess metal curves indicates the absence of binuclear chelates The results are shown in Table 2

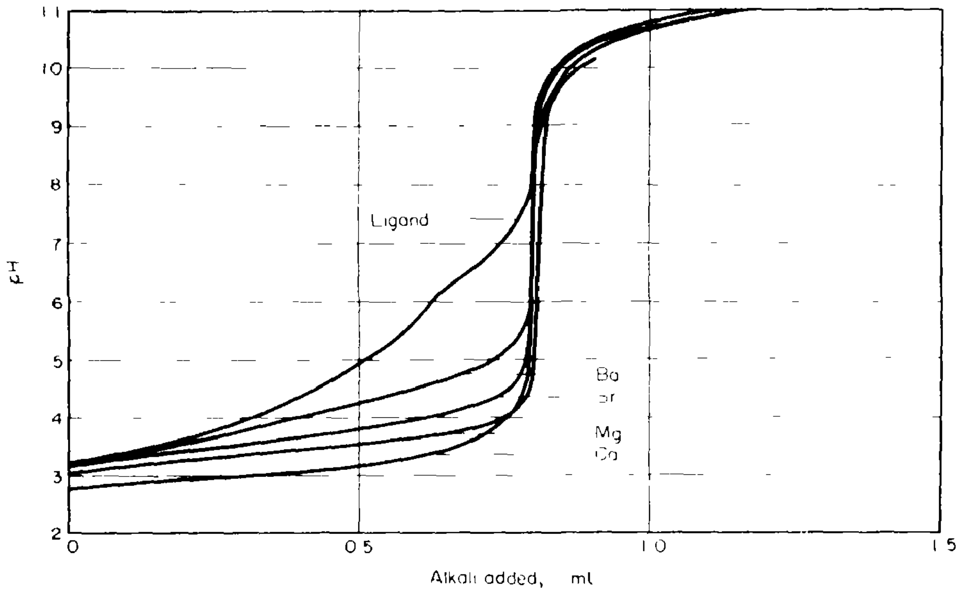


FIG 5 —Titration of *o*-PDTA—metal
Titration of *o*-PDTA in the absence and in the presence of ten times excess of alkaline earth ions

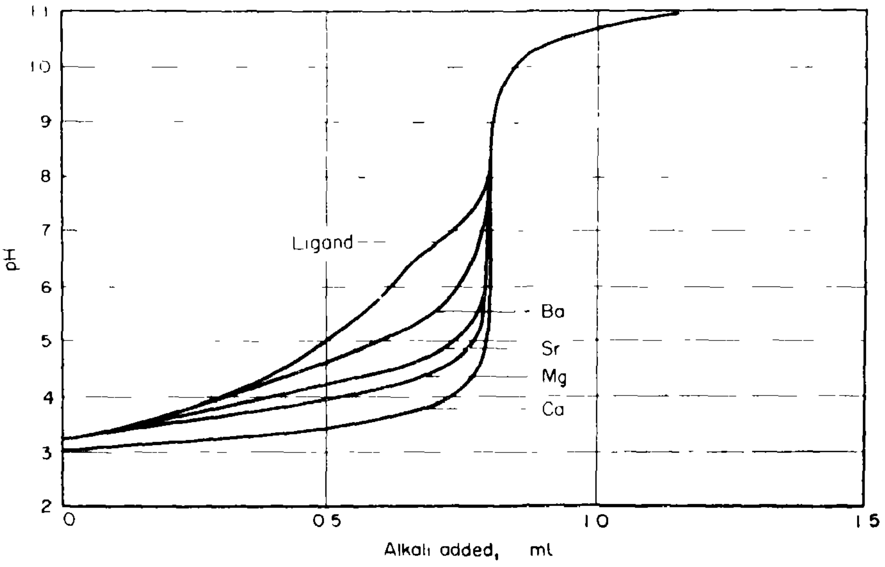


FIG 6 —Titration of *o*-PDTA—metal
Titration of *o*-PDTA in the absence and in the presence of equimolar alkaline earth ions

The results obtained using Irving and Rossotti's(10, 12) method are given in Table 2. The formation curves for the metal–ligand complexes are of normal shape but the results are given to 0.1 log unit only because protonated metal chelates can be shown to be stable intermediates from the data given in Table 2.

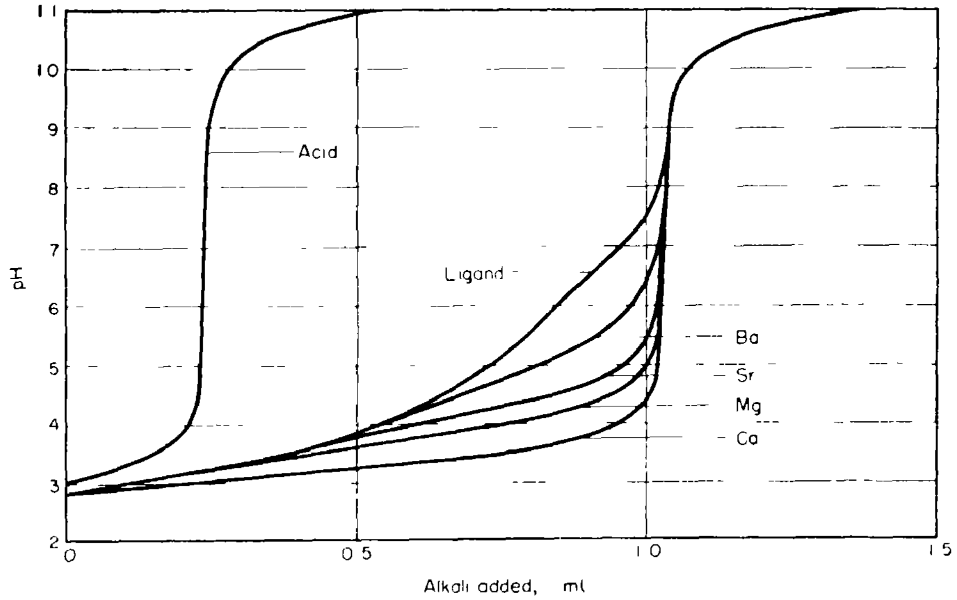


Fig. 7. Titration of o-PDTA–metal.

Titration of o-PDTA, in perchloric acid solution (1 10^{-3} M) in the absence and in the presence of equimolar alkaline earth ions.

For o-PDTA results obtained by the two methods agree well except in the case of calcium, considering the difficulties encountered in calculating the figures in Table 2 and the fact that Irving and Rossotti's method does not take protonated metal chelates into account.

DISCUSSION

For the purpose of comparison, the values of the acid dissociation constants for EDTA, and its chelate stability constants with calcium and with strontium, were measured under the same experimental conditions. The values obtained are shown in Table 1.

Although there is some disagreement about the form of polyaminopolycarboxylic acids in solution(19, 20, 21) it has been assumed throughout that all the compounds studied exist initially in solution as completely betaine forms as proposed by Schwarzenbach and Ackermann.(13)

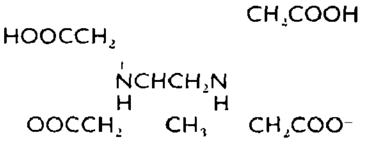
---

(19) D. Chapman, *J. Chem. Soc.* 1766 (1955).

(20) M. J. L. Tillotson and L. A. K. Staveley *J. Chem. Soc.* 3613 (1958).

(21) D. C. Olson and D. W. Margerum, *J. Amer. Chem. Soc.* **82**, 5602 (1960).

Considering first the results for C-Me-EDTA (I)



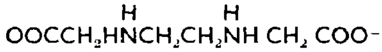
$$\begin{array}{ccc} \mathrm{HOOCCH_2} & & \mathrm{CH_2COOH} \\ & \mathrm{\underset{H}{N}CH(CH_3)CH_2\underset{H}{N}} & \\ \mathrm{OOCCH_2} & & \mathrm{CH_2COO^-} \end{array}$$

I

(N B betaine form)

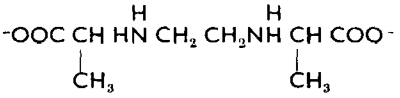
it can be seen that K_1 and K_2, the acid dissociation constants for the two carboxyl protons, are somewhat lower than for EDTA Evidently the inductive effect of the methyl group weakens the electron-withdrawing capacity of the positively charged nitrogen atoms, a similar decrease in acid dissociation constants was observed by Schwarzenbach and Ackermann(22) for 1 2 cyclohexanediamine tetraacetic acid (CDTA)—namely, $pK_1 = 2\ 4$ and $pK_2 = 3\ 5$, both higher than their values for EDTA ($pK_1 = 1\ 99$, $pK_2 = 2\ 67$) CDTA may be regarded as EDTA with two C-substituent alkyl groups joined in a ring There is very little difference between the values of K_3 for C-Me-EDTA and for EDTA, but in the ion where only one positively charged nitrogen is left (i e HL^{3-} in betaine form), the substituent alkyl group has a considerable effect on the ease of removal of the last proton The marked increase in basicity shown in this value for K_4 is reflected in an increase in chelating strength compared with EDTA Smith(14) has reported values of the chelation constants for C-Me-EDTA, but no acid dissociation constants or experimental details were given (See Table 1) These figures do not agree with those published here and the latter have been confirmed by Irving (23)

Comparison of the results for EDDADP with values for EDTA shows that both K_3 and K_4 are smaller for the former Similar increases in nitrogen basicity were reported by Irving *et al* (24) when two compounds—ethylenediamine diacetic acid (II) and ethylenediamine di-(2-propionic acid) (III)—were compared



$$\mathrm{OOCCH_2H\overset{H}{N}CH_2CH_2\overset{H}{N}H\ CH_2\ COO^-}$$

II $pK_1 = 6\ 42$
$pK_2 = 9\ 46$



$$\mathrm{{}^-OOC\ \underset{CH_3}{CH}\ H\overset{H}{N}\ CH_2\ CH_2\overset{H}{N}H\ \underset{CH_3}{CH}\ COO^-}$$

III $pK_1 = 6\ 69$
$pK_2 = 9\ 58$

The increase in nitrogen basicity results in an increase in the stability constant for the calcium chelate of EDDADP compared with EDTA, but not for the strontium chelate—this may be indicative of steric hindrance occurring with the larger metal ion

Some data on the chelating properties of HPDTA have already been reported in the literature(14)—as with C-Me-EDTA only chelate stability constants are given The literature results, together with Schwarzenbach and Ackermann's(11) results for trimethylenediamine-NNN′N′-tetra-acetic acid (TMDTA), are given in Table 1 With the exception of the stability constant for calcium, our results agree well with those quoted by Smith Comparing the results for the acid dissociation constants for

(22) G Schwarzenbach and H Ackermann, *Helv Chim Acta*, 32, 1682 (1949)

(23) H Irving Private communication (1961)

(24) H Irving, R Shelton and R Evans, *Chem Soc* 3540 (1958)

HPDTA and TMDTA, it can be seen that the introduction of a centrally attached hydroxyl group leads to reduced basicity of the nitrogen atoms The two parent amines, 1 3 diaminopropane and 1 3 diaminopropane-2-ol, show a similar effect [9] It is somewhat surprising that in HPDTA the effect is greater for K_3 than for K_4 HPDTA is a weaker chelating agent than TMDTA, but the results are not strictly comparable, as values obtained apply to different temperatures, and our method of calculation takes no account of intermediate protonated metal chelates (SCHWARZENBACH and ACKERMANN[11] have shown that, for tetra-acetic acids based on diamines with two carbon atoms in the main chain, this assumption is justifiable, but that when three carbon atoms interpose between the nitrogen atoms some protonated chelates are present)

The greatly increased acidity of the nitrogen centres of *o*-PDTA compared with EDTA is expected from the presence of an aromatic ring It may be shown empirically by plotting the logarithms of the chelate stability constants for a particular metal against the combined proton affinities of the nitrogen centres ($pK_3 + pK_4$) for several 1,2-diamine tetra-acetic acids, that *o*-PDTA has exceptional chelating ability in relation to its basicity (see Fig 8) This effect must be associated with the presence of a benzene ring, but the explanation is not clear

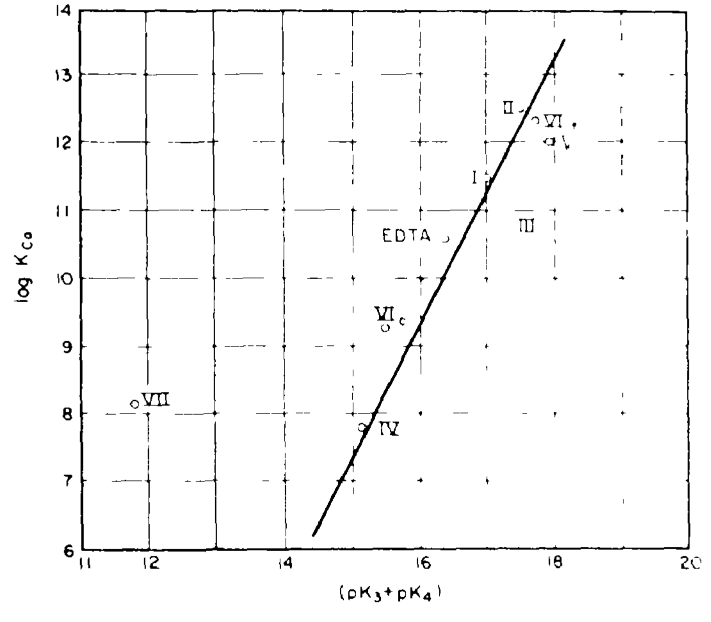


FIG 8 —Plot of log K_{Ca} vs (pK_3 + pK_4) for a number of compounds
I C-Me-EDTA, II 2,3-diaminobutane-NNN′N′-tetraacetic acid III EDDADP IV 1 2-cyclobutanediamine-NNN′N′-tetraacetic acid , V trans-1 2-cyclopentanediamine-NNN′N′-tetraacetic acid , VIc cis-1,2-cyclohexanediamine-NNN′N′-tetraacetic acid VIt trans-1,2-cyclohexanediamine-NNN′N′-tetraacetic acid VII *o*-PDTA

(II) A J HUGGARD and S P WILFORD Unpublished work (IV) and (V) V G YASHUNSKII, *J Gen Chem* (USSR) **28**, 1026 (1958) (VIc) H KROLL and M GORDON, *Abstr Amer Chem Soc Meeting*, New York (September 1960) (VIt) V G YASHUNSKII and M N SHCHUKINA, *J Gen Chem* (USSR) **28**, 230 (1958)

The values of the acid dissociation constants for CTHA are as expected for a hexa-acetic acid based on a triamine—i.e. three strongly acidic protons and three betaine protons. The considerable stability of the chelate M_2L, compared with the stability of the chelate ML (i.e. for CTHA, $\log K_{CaL} - \log K_{Ca_2L} = 1.9$ whereas for TTHA, $\log K_{CaL} - \log K_{Ca_2L} = 6.0$), and the relatively low value of the chelate stability constants for the chelate ML, suggest that the three iminodiacetic acid groupings are not all operative in forming the latter. This implies that the CTHA molecule exists in solution as the triequatorial form, the energy released when a chelate is formed being insufficient to cause a change to the triaxial form which might be expected to give a a more stable chelate (since CTHA exists in solution in a tri-betaine form, a considerable energy difference between the tri-axial and tri-equatorial forms will exist owing to the mutual repulsion of the positively charged nitrogen centres).

The acid dissociation constants for TTHA agree reasonably well with those obtained by FROST,(25) allowing for the difference in temperature. Examination of the titration curves for TTHA with equimolar metal present (Fig. 3) indicates that the magnesium curve intersects both the strontium and the barium curves. These intersections are due to the greater acidities (as shown by K^{H}_{MHL}) of the protonated strontium and barium chelates compared to the corresponding magnesium chelate. It can be shown, using Equation (13) that, depending on the relative magnitudes of K^{H}_{MHL} and K_{MHL}, this may lead to a reversal of affinity orders. Thus with the magnesium and strontium chelates it is found that $K_{SrL} > K_{MgL}$ although $K_{MgHL} < K_{SrHL}$, but no such reversal occurs for magnesium and barium. It is evident that some effect must operate on the release of the last proton which is relatively less favourable for the magnesium chelate than for the chelates of strontium and of barium—possibly a steric effect connected with the small size of the magnesium ion (radius 0.66 Å), as compared to the strontium ion (radius 1.18 Å) and the barium ion (radius 1.34 Å), and the ensuing mutual repulsion of donor groups. DURHAM and RYSKIEWICH(26) found analogous results with diethylenetriamine-penta-acetic acid (DTPA). A similar effect is found for the calcium curve, which intersects both the strontium and the barium curves, but as in the magnesium/barium case this does not lead to any reversal of affinity orders.

In conclusion it may be said that the results of this study agree well with the known chelate stability orders for the alkaline earth metals. That is, for calcium, strontium and barium the order is invariably $K_{Ca} > K_{Sr} > K_{Ba}$, but as has been noted previously, the position of magnesium is not fixed.

Acknowledgements.—We thank DR. P. J. A. SMITH, MESSRS. D. C. MAXWELL and J. R. MORRIS and MRS. F. BRYAN for assistance with the experimental work, the analytical section for analyses, and MR. K. T. B. SCOTT and PROF. H. IRVING for helpful discussions. We also thank DR. J. K. AIKEN and the Geigy Company Ltd. for gifts of chelating agents.

(25) A. E. FROST, *Nature, Lond.* **178**, 322 (1956).

(26) E. J. DURHAM and D. P. RYSKIEWICH, *J. Amer. Chem. Soc.* **80**, 4812 (1958).

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 1239 to 1243. Pergamon Press Ltd. Printed in Northern Ireland

THE COMPLEX FORMED BETWEEN THE 5-TRIFLUOROMETHYL-TETRAZOLYL ION AND SOME TRANSITION METAL IONS*

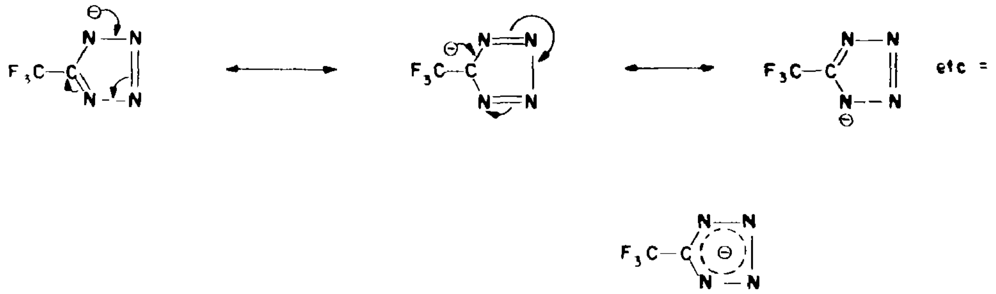
H. B. JONASSEN,† J. O. TERRY,‡ and A. D. HARRIS†
Richardson Chemistry Laboratory, Tulane University, New Orleans, Louisiana

(*Received* 8 *March* 1963, *in revised form* 19 *April* 1963)

Abstract—The 5-trifluoromethyltetrazolyl anion has been shown to be a weakly co-ordinating ligand in aqueous solutions. The cations used in this investigation were $[Co(H_2O)_6]^{2+}$, $[Ni(H_2O)_6]^{2+}$ and $[Cu(H_2O)_4]^{2+}$. The anion is unable to displace any water molecules from the first coordination sphere of the $[Co(H_2O)_6]^{2+}$ ion. Two water molecules can be displaced from the hydrated Ni(II) ion and a weakly bonded $[Ni(H_2O)_4][C_2N_4F_3]_2$ complex is formed. The $[Cu(H_2O)_4]^{2+}$ ion forms a rather stable monohydrated complex containing two $C_2N_4F_3$ ions. The stoicheiometry of the reaction was studied by both spectrophotometric means and continuous variations studies. Magnetic susceptibility and infrared data seem to confirm these conclusions.

SODIUM 5-trifluoromethyltetrazole,⁽¹⁾ a partially aromatic compound, is of interest as a coordinating ligand since its electronic structure, neglecting the lone pair of electrons on each nitrogen atom, is very similar to the cyclopentadienyl anion.

FINNEGAN and coworkers⁽²⁾ have studied the formation of 5-substituted tetrazoles and found that electronegative groups on the nitrile used as starting materials facilitate the production of a tetrazole ring by stabilizing the negatively charged intermediate. The negative charge can be delocalized into the ring by the strongly electron withdrawing nature of the —CF_3 group in the following manner.⁽¹⁾



Since delocalization of the negative charge into the ring gives the ring an aromatic sextet, utilization of the —CF_3 group as a substituent in the 5-position has increased the tetrazole ring's coordinating ability. Also since the trifluoromethyltetrazolyl anion has a π-cloud, the possibility exists that this π-cloud will interact with metal ions to produce either π-complexes or normal addition complexes This paper reports on the reactions of this anion with Cu(II), Co(II), and Ni(II) ions

---

* Presented at the Southwide Regional Meeting of the American Chemical Society, New Orleans, La. December 1961.

† Tulane University, New Orleans, Louisiana.

‡ National Science Foundation, Undergraduate Research Participant, Tulane University, Louisiana, 1959–61.

⁽¹⁾ W. P. NORRIS, *J. Org. Chem.* **27**, 3248 (1962).

⁽²⁾ W. G. FINNEGAN, R. A. HENRY and R. LOFQUIST, *J. Amer. Chem. Soc.* **80**, 3908 (1958).

EXPERIMENTAL

The chemicals used in this investigation were reagent grade The sample of sodium 5-trifluoromethyltetrazole was prepared by NORRIS,[1] whose generosity in supplying this compound is gratefully acknowledged

Analytical methods

The per cent copper was determined by electrodeposition however cobalt was determined by direct titration using EDTA and pyrogallol red Nickel was determined gravimetrically using dimethylglyoxime as the precipitant Samples for analysis were decomposed by treatment with a mixture of nitric and perchloric acids

Determinations of C, H, and N were performed by A BERNHARDT *

Preparation of complexes

Copper(II) complex $Cu(C_2N_4F_3)_2$ H_2O To 100 ml of an aqueous solution of 8 55 g of $CuCl_2$ $2H_2O$ were added 8 g of $NaC_2N_4F_3$ After standing for 1 hr a blue fibrelike precipitate resulted This solid, when dried over $CaCl_2$, contained about four waters of hydration Drying the blue precipitate to constant weight *in vacuo* over P_2O_5 yielded the blue monohydrate Gas chromatographic analysis showed that during the drying process only water was lost (Found C, 13 2, N, 31 5, Cu, 17 5 Calc for $Cu(C_2N_4F_3)_2$ H_2O C, 13 5, N, 31 6, Cu, 17 8%)

Cobalt(II) complex $Co(C_2N_4F_3)_2$ $6H_2O$ Five grammes of $NaC_2N_4F_3$ were added to 50 ml of an aqueous solution of 4 5 g of $Co(NO_3)_2$ $6H_2O$ Almost immediately a yellow amorphous precipitate formed On drying *in vacuo* over P_2O_5, the complex lost water and changed from yellow to a red brown, however no constant weight value could be obtained This red brown form turned yellow on exposure to moisture (Found C, 11 1, N, 25 7, Co, 13 7 Calc for $Co(C_2N_4F_3)_2$ $6H_2O$ red brown, C, 10 9, N, 25 4, Co, 13 4%)

Nickel(II) complex $Ni(C_2N_4F_3)_2$ $4H_2O$ To 100 ml of an aqueous solution containing 11 4 g of $Ni(ClO_4)_2$ $6H_2O$ were added 5 0 g of $NaC_2N_4F_3$ After standing for several days a pink amorphous precipitate formed The yield of complex was increased by salting out the precipitate using $NaNO_3$ After drying *in vacuo* over P_2O_5, this pink precipitate became violet in colour (Found C, 12 0, N, 27 0, Ni, 14 7 Calc for $Ni(C_2N_4F_3)_2$ $4H_2O$ C, 11 9, N, 27 6, Ni, 14 5%)

Preparations in nonaqueous media Ethanolic solutions of both $Cu(C_2H_3O_2)_2$ H_2O and $CuCl_2$ $2H_2O$ were reacted with solutions of $NaC_2N_4F_3$ A blue green material resulted with the $Cu(C_2H_3O_2)_2$ and a pale green precipitate with the $CuCl_2$ The addition of water yielded a blue precipitate, however no constant analyses could be obtained for these complexes The precipitate obtained was not the fibrelike form obtained from water solution Attempts with the Ni(II) and Co(II) ions gave similar results

Spectrophotometric studies of the complexes

Aqueous solutions (a) Copper(II) To 0 05F solutions of $CuCl_2$ and $Cu(NO_3)_2$ were added a 0 05F solution of sodium 5-trifluoromethyltetrazole in a ratio of 1 1, 1 2 and 1 3, and their visible spectra studied with the Beckman DB Spectrophotometer The spectra indicated a shift in the maxima from 725 mμ to 712 mμ for the ratio of 1 2 No further change occurred at the 1 3 ratio An isobestic point was observed at 395 mμ

(b) Cobalt (II) Solutions of $CoCl_2$ and sodium 5-trifluoromethyltetrazole of 0 1F concentration were reacted in the same manner A yellow precipitate occurred and no information could be obtained from the spectra In dilute solutions of 0 02F or less concentration, no shifts in spectra could be observed

(c) Nickel(II) Solutions 0 1F in $Ni(ClO_4)_2$ and $NaC_2N_4F_3$ were reacted in the same manner A colour change from green to violet was observed A spectrum for the visible region showed three isobestic points at 600 mμ, 475 mμ and 375 mμ As complexing occurred, two maxima appeared at 525 mμ, and 330 mμ

---

* Microanalytisches Laboratorium im Max Planck Institute fur Kohlenforschung, Mulheim Germany

Alcoholic solutions (a) Copper(II) Chloride Solutions 0 05F in both $CuCl_2$ and $NaC_2N_4F_3$ were reacted in the same manner A colour change from olive green to emerald green for the ratio of 1 1 to blue for the ratio of 1 2 and 1 3 was observed No further change was found as the ratio decreased An isobestic point at 620 mμ was also detected

(b) Cobalt(II) nitrate A solution of 0 1F in $Co(NO_3)_2$ was reacted in the same manner A colour change was observed from red in the unreacted solution to orange yellow at the ratios of 1 2 and 1 3 The solution showed a shift in the maxima from 515 mμ to 482 mμ at the ratio of 1 2 No further shift was detected as the ratio decreased An isobestic point was observed at 328 mμ

(c) Nickel(II) perchlorate Solutions 0 1F in both reactants were studied in the same manner A colour change from green to violet was observed A maxima at 570 mμ appeared as complexing occurred A shift in the maxima from 395 mμ for unreacted nickel perchlorate to 360 mμ for the ratio of 1 2 was observed An isobestic point was detected at 475 mμ

Continuous variation and mole ratio study The Continuous Variation and Mole Ratio method was applied to a study of the complexes of the copper(II), nickel(II), and cobalt(II) ion with the trifluoromethyltetrazole ion Solutions 0 1F were used at the various wavelengths for the Ni(II) complex Since a solution 0 1F in Co(II) and in trifluoromethyltetrazole anion gave a precipitate these solutions were diluted to 0 02F For the study of the copper complexes 0 05F solutions were used

Infra-red study The infra-red spectra of $NaC_2N_4F_3$ and the Cu(II), Ni(II), and Co(II) complexes of trifluoromethyltetrazole were obtained using the KBr disc method with a Beckman IR5 infra-red spectrophotometer The results are given in Table 1

Magnetic susceptibility measurements

The magnetic susceptibility measurements were obtained by standard Gouy procedure using a semi-micro analytical balance and a permanent magnet having a field strength of 4,500 G

RESULTS AND DISCUSSIONS

Spectral studies

The interaction of the three transition metal ions with the tetrazole anion was studied in aqueous and in some cases alcoholic solutions by the Continuous Variation and Mole Ratio methods Visible absorption spectra indicated complex formation in both media The studies for both the Cu(II) ion and Ni(II) ion indicate that a 1 2 complex forms under these conditions

The Cu(II) ion was studied at λ - 670 mμ and a graph of these data is shown in Fig 1 For the Ni(II) ion a λ — 330 mμ was used and these data are shown in Fig 2

Since solutions 0 1F in both $Co(NO_3)_2$ and the tetrazole anion are sufficiently concentrated to cause precipitation, solutions diluted to 0 02F were used However, in dilute aqueous solutions no interaction could be observed between the tetrazole and the Co(II) ion When repeated in alcoholic solution a maximum was observed at 450 mμ in 0 1F solution at a ratio of 1 2 Similar results were obtained by the Mole Ratio method

Infra-red spectra (*Table* 1)

A broad band was observed in the 1640–1625 cm^{-1} region which seems to be the shifted water deformation frequency Since it was shifted to a higher frequency in the copper(II) complex it appears that the tetrazoles π-cloud interferes with the in-plane deformation most in the Cu(II) complex, possibly due to hydrogen bond formation (3) This band practically disappears in the nearly anhydrous complex formed from ethanolic solution

---

(3) G C Pimentel and A L McClellan, *The Hydrogen Bond*, p 118 Freeman, San Francisco (1960)

In Ni(II) and Co(II) complexes, H_2O seems to be bonded to the metal ion since only a very slight shift of the band in this region is observed

The 1505 1500 cm $^{-1}$ band is the C--CF_3 stretching frequency whereas that at 754 747 cm $^{-1}$ seems to be the CF_3 deformation frequency (4)

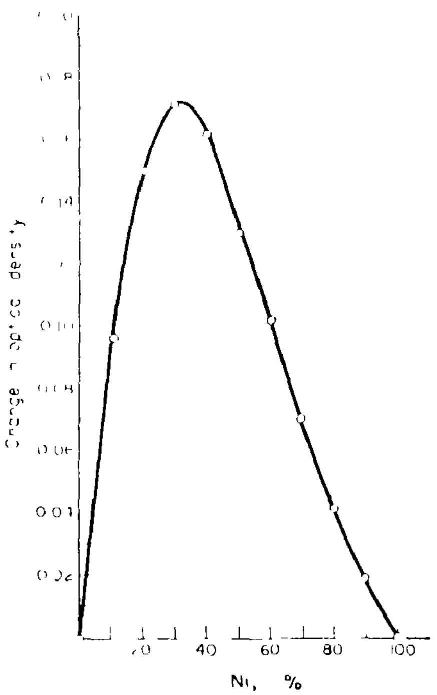


Fig. 1 --Continuous variation study $Cu(NO_3)_2$ with $NaC_2N_4F_3$ 0 05 F in H_2O

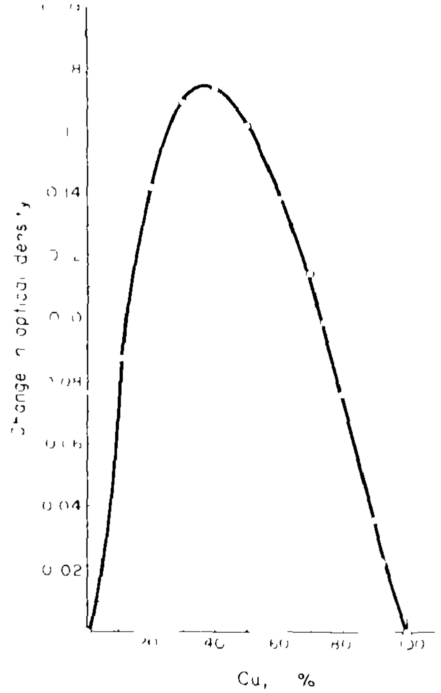


Fig. 2 --Continuous variation study $Ni(ClO_4)_2$ with $NaC_2N_4F_3$ 0 1 F in H_2O

Table 1 -Infra-red absorption (in cm $^{-1}$) of the trifluoromethyltetrazole ion and the Cu(II), Ni(II), and Co(II) complexes

$NaC_2N_4F_3$	$Cu(C_2N_4F_3)_2$ H_2O	$Ni(C_2N_4F_3)_2$ $4H_2O$	$Co(C_2N_4F_3)_2$ $6H_2O$
1640 (*s*)	1625 (*m*)	1635 (*s*)	1635 (*m*)
1500 (*s*)	1500 (*s*)	1505 (*s*)	1505 (*m*)
1415 (*w*)	1410 (*s*)	1410 (*w*)	
		1381 (*s*)	1385 (*s*)
1232 (*w*)	1265 (*w*)	1260 (*m*)	1250 (*w*)
	1210 (*br*)	1215 (*sh*)	1205 (*w*)
1187 (*br*)	1178 (*br*)	1178 (*br*)	1180 (*br*)
1167 (*br*)		1155 (*br*)	1156 (*sh*)
1136 (*br*)		1120 (*w*)	
		1090 (*w*)	
1072 (*vw*)	1075 (*s*)	1072 (*sh*)	1069 (*w*)
1038 (*s*)	1034 (*s*)	1040 (*w*)	1039 (*m*)
			835 (*w*)
772 (*w*)	776 (*m*)	776 (*w*)	774 (*w*)
747 (*m*)	754 (*s*)	754 (*s*)	754 (*m*)

(*s*) strong, (*m*) medium, (*w*) weak absorption, (*br*) broad, (*sh*) shoulder

(4) L J Bellamy, *The Infra-red Spectra of Complex Molecules* (2nd Ed) p 332. Methuen, London (1958)

The band from 1260–1136 cm^{-1} can be assigned to the C—F stretching frequency (5) The assignment of individual frequencies becomes difficult because of the intense nature of the fluoro-carbon bond The 1410–1385 cm^{-1} band appears to be the N=N bond

The bands from 1041–1033 cm^{-1} and 1075–1069 cm^{-1} are the skeletal region of the tetrazole (6) A shift to lower frequency is observed in the 1033–41 cm^{-1} region for the Co(II) and the Ni(II) complex while in the Cu(II) complex a shift to higher frequency is found This shift, although small, again seems to indicate some interaction between Cu(II) ion and the tetrazole ring's π-cloud

Magnetic susceptibility studies (*Table* 2)

The magnetic data seem to confirm the infra-red assignments In the Co(II) complex the hydrated metal ion shows the expected moment for d^2sp^3 co-ordination (7) Little effect on the moment of this hydrated ion would be expected from a non-coordinating tetrazolyl ion However, in the Ni(II) ion the tetrazolyl ion seems to participate in bonding to give sp^3d^2 hybridization (8) The slight changes in tetrazole infra-red frequencies seem to substantiate this

TABLE 2 MAGNETIC MEASUREMENTS

μ_{eff} $2\ 839\sqrt{(\chi m_{corr} T)}$

Compound	χm_{corr}		T (K)	μ_{eff}(obs)
$Co(C_2N_4F_3)_2\ 6H_2O$	10 894	10^{-6}	300	5 1
$Ni(C_2N_4F_3)_2\ 4H_2O$	3 550	10^{-6}	298	2 8
$Cu(C_2N_4F_3)_2\ H_2O$	1 653	10^{-6}	298	2 0

The moment of the Cu(II) complex indicates strong interaction The magnetic moment was found to be higher than that expected for dsp^2 or d^2sp^3 bonding indicating possibly a change toward tetrahedral configuration with the two tetrazolyl ions occupying the four co-ordinating positions in the complex (9)

General observations

This work indicates that this tetrazolyl ion can participate in coordination with some transition metal ions (10)

The Cu(II) complex precipitates from aqueous solution as long needles indicating possible polymerization as previously observed by BRUBAKER for other tetrazole complexes

The solubility of the complexes seems to be higher in organic solvents than most tetrazole complexes previously reported

Further work with tetrazoles is under way

Acknowledgements—We thank Dr E BOUDREAUX for the magnetic susceptibility measurements, Dr W P NORRIS, Chemistry Division U S Naval Ordnance Test Station China Lake, and Dr J FANNING for helpful discussions Partial financial support by the Office of Naval Research is gratefully acknowledged

(5) L J BELLAMY, *The Infra-red Spectra of Complex Molecules* (2nd Ed) p 332 Methuen, London (1958)

(6) I LIEBER, D LEVERING and L PATTERSON *Analyt Chem* **23**, 2594 (1951)

(7) P W SELWOOD, *Magneto Chemistry* p 225 Interscience, New York (1956)

(8) P W SELWOOD, *Magneto Chemistry*, p 225 Interscience New York (1956)

(9) P SELWOOD, *Magneto Chemistry*, p 235 Interscience, New York (1956)

(10) N A DAUGHERTY and C H BRUBAKER, *J Amer Chem Soc* **83**, 3779 (1961)

J Inorg Nucl Chem 1963, Vol 25, pp 1245 to 1252 Pergamon Press Ltd Printed in Northern Ireland

A KINETIC STUDY OF THE ISOTOPIC EXCHANGE OF INDIUM BETWEEN THE INDIUM ION AND ITS ETHYLENEDIAMINE-N,N,N′,N′-TETRA-ACETATE IN WATER

K Saito and M Tsuchimoto
Institute for Nuclear Study, University of Tokyo, Tanashi, Tokyo, Japan

(*Received* 21 *March* 1963)

Abstract—Isotopic exchange of indium between the indium ion and its EDTA complex is immeasurably slow in neutral solution and very fast in strongly acid and basic solutions. The rate is measurable in the pH regions near 2 and 10, and the rate constant for exchange is independent of the concentration of uncomplexed indium and proportional to that of the complex. In basic media the rate constant is proportional to $[OH^-]^2$ with an Arrhenius activation energy of 25 kcal mole^{-1}. At pH 1 to 2 the rate constant is proportional to $[H^+]^3$ with an activation energy of 18 kcal mole^{-1}. The complex appears to be more inert than the corresponding gallium complex.

Our kinetic study of isotopic exchange involving co-ordination compounds with the d^{10} electronic structure has been extended to indium, using as tracer ^{114m}In. We have found the exchange of indium between the indium ion and its ethylenediamine-N,N,N′,N′-tetra-acetate (henceforth written as EDTA with the formula given by H_4Y) to be very slow in neutral and weakly acid solutions, but very fast in basic and strongly acid solutions. The exchange rate is measurable at pH values near 10 and 1.5, and may be expressed by McKay's formula

$$R = -\frac{2.303\,ab}{a+b}\cdot\frac{\log(1-F)}{t}$$

where t is the time in seconds, F the fractional exchange, and a and b represent the concentrations of uncomplexed indium (initially inactive) and the indium complex (active) respectively. This paper deals with the kinetics in these regions and compares them with those for the corresponding gallium complex.(1) The kinetics differ appreciably in the acid and basic regions and are discussed separately below.

RESULTS AND DISCUSSION

Isotopic exchange in weakly basic solution. The rate of exchange R is independent of the concentration of uncomplexed indium a, for different buffers such as barbiturate, glycine and p-oxy-benzoic acid (Table 1). On the other hand, it is proportional to the concentration of the indium complex, b, and the rate constant k, expressed by R/b, has the dimensions t^{-1}. Fig. 1 illustrates the relationship between k and the OH^- ion concentration in various buffer solutions. It will be seen that the exponent x in the equation $k = k'\,[OH^-]^x$ is highly dependent on the buffering agent, x is equal to two in barbiturate and p-oxybenzoate, and the

---

(1) K. Saito and M. Tsuchimoto, *J. Inorg. Nucl. Chem.* **23**, 71 (1961).

TABLE 1.—RELATIONSHIP BETWEEN EXCHANGE RATE AND THE CONCENTRATIONS OF UNCOMPLEXED INDIUM AND INDIUM EDTA COMPLEX IN WEAKLY BASIC SOLUTION

a (10^{-3} M)	*b* (10^{-3} M)	R_0 (10^{-8} mole l^{-1} sec^{-1})	*k* (10^{-5} sec^{-1})
0.65	1.20	4.2	3.5
1.20	1.20	4.8	4.0
1.96	1.20	4.5	3.8
1.20	0.72	2.9	4.0
1.20	1.92	6.9	3.6

μ = 0.30 (KNO_3), 25°C, 0.060 M tartrate and 0.0375 M barbiturate, pH, 10.98

a (10^{-3} M)	*b* (10^{-3} M)	R_0 (10^{-8} mole l^{-1} sec^{-1})	*k* (10^{-5} sec^{-1})
0.76	1.18	7.6	6.4
1.06	1.18	7.9	6.7
1.36	1.18	8.0	6.8
1.67	1.18	7.9	6.7
1.21	0.48	2.9	6.0
1.21	0.97	6.6	6.8
1.21	1.44	10.1	7.0
1.21	1.93	13.3	6.9

μ = 0.32 (KNO_3), 25°C, 0.060 M tartrate and 0.050 M glycine, pH, 9.76

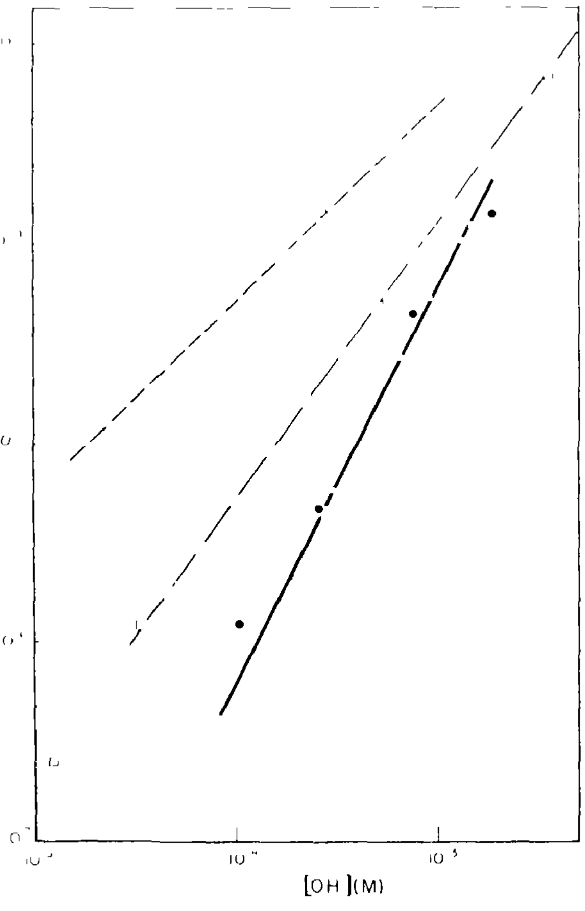


FIG. 1.—Relationship between *k* and [H^+] in basic solutions buffered by various agents μ = 0.32 (KNO_3), 25°C, *a*, 1.20 × 10^{-3} M, *b*, 1.34 × 10^{-3} M, tartrate, 0.060 M, solid line in 0.0375M barbiturate (○) and in *p*-oxybenzoate 0.0125 M (●), broken line in 0.0625 M glycine, dotted line in 0.2 M NH_3 solution containing 0.032 M NH_4NO_3, the pH being adjusted with 2N HNO_3 and KOH solution

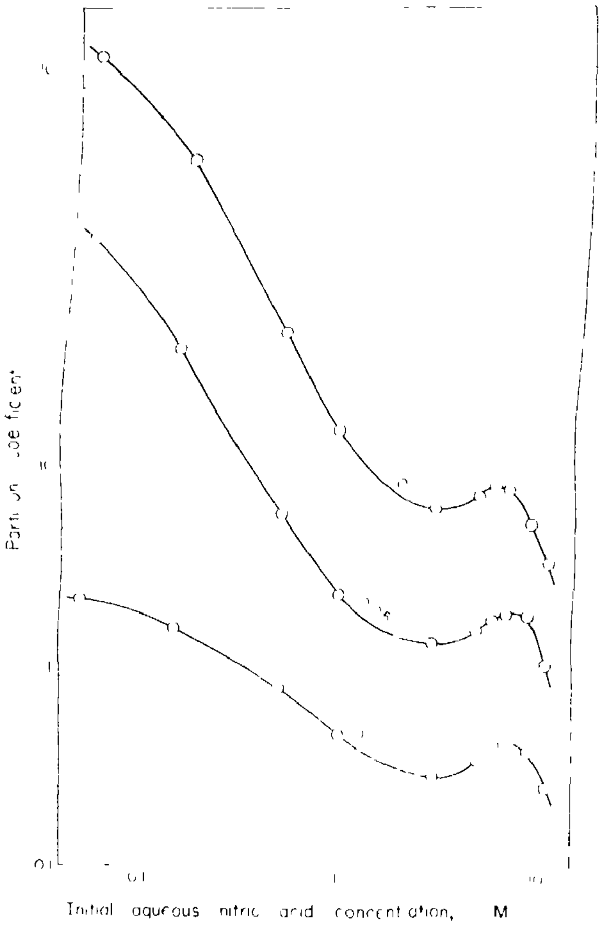


FIG. 1. Variation of partition coefficient with nitric acid concentration for the extraction of uranium (VI) by solutions of DEHPA in kerosene (figures on curves are DEHPA concentrations, M) $UO_2(NO_3)_2$ 5g/l 20°C

If we assume that the initial decrease in partition coefficient shown in Fig. 1 is governed by an ion-exchange reaction similar to that in the extraction of uranium (VI) from sulphuric acid solution by DEHPA,[6] viz

$$UO_2^{2+}(a) + 2(HX)_2(o) \rightleftarrows UO_2X_4H_2(o) + 2H^+(a), \tag{1}$$

where X represents the anion $(C_8H_{17}O)_2PO_2^-$, while (a) and (o) are indicative of aqueous and organic phases respectively, then the following relationship would be obtained

$$\log 4L_u' = \log K + 2\log(C_s - 4C_U)/C_H, \tag{2}$$

where L_u' is the partition coefficient, K the equilibrium constant, C_s the total DEHPA concentration C_U the organic phase uranium concentration and C_H the aqueous acidity. However, when values of $\log F_a^0$ were plotted vs $\log(C_s - 4C_U)/C_H$ in

---

[6] C. A. BLAKE Jr., C. F. BAES, Jr., K. B. BROWN, C. F. COLEMAN and J. C. WHITE, *The Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958 Vol 28, p 289 United Nations (1958)

k' values are almost identical. In glycine solution x equals unity and the exchange rate is measurable at a much lower pH. Table 2 shows the influence of the concentration of the buffering agents together with that of ionic strength. Whilst the concentration of barbiturate and of *p*-oxybenzoate has little effect on k', the latter increases with increasing concentration of glycine. In both cases, and influence of ionic strength is very small. The temperature dependence of k' is shown in Fig. 2, from which the Arrhenius activation energies are calculated.

TABLE 2.—INFLUENCE OF BUFFER AND MASKING AGENT AND OF IONIC STRENGTH UPON THE EXCHANGE RATE

Concn. of reagents (M)			μ	k'*
Tartrate 0.060	Barbiturate	0.025	0.32	45
0.060		0.0375	0.32	44
0.043		0.0375	0.32	52
0.060		0.0375	0.40	53
0.060		0.100	0.32	45
0.060	*p*-oxy-benzoate	0.0125	0.32	53†
Tartrate 0.060	Glycine	0.025	0.32	0.31
0.060		0.050	0.32	0.68
0.158		0.050	0.32	0.59
0.060		0.050	0.010	0.65
0.060		0.050	0.55	0.69
0.060		0.050	0.032‡	0.75
0.060		0.375	0.032	0.76

a, 1.20 × 10^{-3} M, *b*, 1.20 × 10^{-3} M at 25°C.

* The dimensions of k' are l mole^{-1} sec^{-1} for the results in barbiturate and *p*-oxybenzoate buffer and l^2 mole^{-2} sec^{-1} for those in glycine buffer.

† Change in concentration of *p*-oxybenzoate does not affect the rate (results omitted).

‡ The ionic strength was adjusted with KCl (others with KNO_3).

The results show that the mechanism differs slightly from that for the gallium EDTA complex. In basic solutions indium which is not complexed with EDTA will be present as the tartrate complex, but its state is not important in discussing the reaction mechanism, since the rate of exchange is independent of its concentration a and of that of total tartrate. The indium EDTA complex has one co-ordinated water molecule, which dissociates slightly to give the hydroxyl complex $[InY OH]^{2-}$ with an apparent dissociation constant 1.6 × 10^{-9} at 25°C., at pH 10 the complex is largely present in the hydroxy form. The co-ordinated water may be replaced by other ligands, e.g. by NH_3 in ammoniacal solution. In solutions buffered with barbiturate and *p*-oxybenzoate, the rate constants are very similar and are independent of the concentration of the buffering agents, despite their different molecular structures. Hence in these solutions the exchange must involve the dissociation of the hydroxy-EDTA complex of indium as the rate-determining step and these buffering agents would not replace the co-ordination water under the given conditions.

In Table 3 the kinetic data are compared with those for the aquated EDTA and EDTA-OH (N-2-hydroxyethylethylenediamine-N,N′,N′-triacetate, formulated as H_3Z)

TABLE 3. COMPARISON OF KINETIC DATA AT 25°C

	$[\mathrm{GaY\,OH_2}]^-$	$[\mathrm{GaZ\,OH_2}]$	$[\mathrm{InY\,OH_2}]^-$
K_2	1.2×10^{-6}	1.5×10^{-5}	1.6×10^{-9}
k	$k'\,[\mathrm{OH^-}]$	$k'\,[\mathrm{OH^-}]$	$k'\,[\mathrm{OH^-}]^2$
k'	11.3 (l mole^{-1} sec^{-1})	37 (l mole^{-1} sec^{-1})	52 (l^2 mole^{-2} sec^{-1})
E_A kcal mole^{-1}	25	27	25
k at pH 10	*1.1×10^{-3}	*3.4×10^{-3}	1.2×10^{-6}

* Calcd from k'

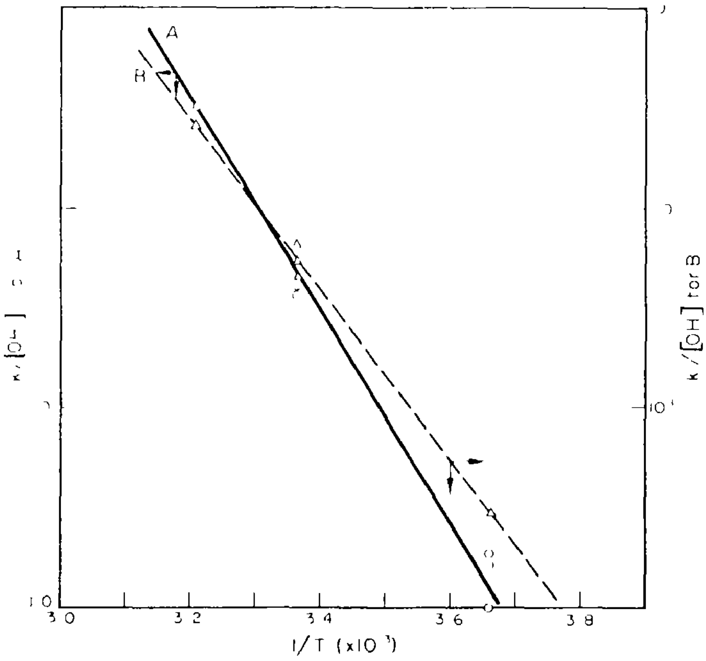


FIG. 2.—Temperature dependence of k in basic media. $\mu = 0.32$ ($\mathrm{KNO_3}$), a, 1.21×10^{-3} M, 25°C, b, 1.21×10^{-3} M, tartrate, 0.060 M, solid line in 0.0375 M barbiturate, broken line, in 0.0625 M glycine.

complexes of gallium. The rate appears to increase in the sequence $[\mathrm{InY\,OH_2}]^-$, $[\mathrm{GaY\,OH_2}]^-$, $[\mathrm{GaZ\,OH_2}]$, which is consistent with the increase in the apparent acid dissociation constant K_2 of the co-ordinated water.[2] If K_2 is regarded as a measure of the affinity between the central metal ion and the co-ordinated water molecule the lability of these complexes may be correlated with the ease with which the conjugate base is formed by the action of $\mathrm{OH^-}$ ion. The indium complex would be so inert that the conjugate base $[InY\,O]^{3-}$ is not sufficiently labile, and requires further attack by another OH^- ion for the following exchange to take place.

---

[2] K. SAITO and H. TERREY, *J. Chem. Soc.* 4701 (1956).

$$[{}^*InY\,OH]^{2-} + OH^- \rightleftarrows [{}^*InY\,O]^{3-} + OH_2$$

$$[{}^*InY\,O]^{3-} + OH^- \rightleftarrows [{}^*InY\,O\,OH]^{1-}$$

$$[{}^*InY\,O\,OH]^{1-} + [In\,tart]^{n} \rightleftarrows [InY\,O\,OH]^{1-} + [{}^*In\,tart]^{n}$$

The kinetic data may alternatively be interpreted if we assume the presence of another molecule of co-ordinated water with dissociation constant much smaller than 1.6×10^{-9} at 25°C which is not detectable potentiometrically. HOARD, SMITH and LIND have suggested a "distorted crystal structure" with co-ordination number seven for solid aquated EDTA complexes of some tervalent metals including iron, and the rare earth elements,(3) and if the indium EDTA complex could assume a distorted form in aqueous solution, the formation of such intermediates would not be unreasonable.

The greater value of k' and the smaller value of x in glycine solutions suggest that the dissociation is facilitated by the presence of glycine, which can replace the coordinated water to give a more labile complex at pH 9–10, where a significant amount of glycine is present as glycinate ion.

$$[{}^*InY\,OH_2]^- + NH_2CH_2CO_2^- \rightleftarrows [{}^*InY\,NH_2CH_2CO_2]^{2-} + H_2O$$

Even when the OH^- ion concentration is in the range 10^{-6} to 10^{-5} M, the conjugate base formed from the glycine complex would dissociate, leading to measurable isotopic exchange with the tartrate complex of indium.

$$[{}^*InY\,NH_2CH_2CO_2]^{2-} + OH^- \rightleftarrows [{}^*InY\,NHCH_2CO_2]^{3-} + H_2O$$

$$[{}^*InY\,NHCH_2CO_2]^{3-} + [In\,tart]^{n} \underset{\text{rapid}}{\overset{\text{slow}}{\rightleftarrows}} [InY\,NHCH_2CO_2]^{3-} + [{}^*In\,tart]^{n}$$

In an ammoniacal solution at pH 9–11.5 the plot of log k vs log $[OH^-]$ is linear, with an apparent value of $x = 1.4$. In this region the ammonia complex $[InY\,NH_3]^-$ would predominate, but the individual influence of the concentrations of OH^- ions and of ammonia could not be measured, because the NH_3 concentration increases as the pH is increased. Nevertheless, the rate is greater than that in barbiturate or *p*-oxybenzoate solutions involving the hydroxy complex $[InY\,OH]^{2-}$, nitrogen co-ordination appearing to facilitate isotopic exchange. On the other hand, the use of azide ions as buffer gave results similar to those with barbiturate.

Isotopic exchange in strong acid solution. The exchange rate is immeasurably small in acid solution at pH > 2.0, but increases remarkably with increasing hydrogen ion concentration. The dependence of R upon a and b is shown in Table 4. The log–log plot in Fig. 3 indicates that $k = R/b$ is proportional to $[H^+]^3$ from pH 1–2 at the given ionic strength and temperature. The Arrhenius activation energy E_A, calculated from Fig. 4 is 17.6 kcal mole^{-1}, and the effect of ionic strength is slight. The rate incréases linearly with increase in chloride concentration, (see Fig. 5) remaining proportional to $[H^+]^3$. E_A (12.8 kcal mole^{-1}) is significantly smaller in the presence of chloride (Fig. 4).

The mechanism is therefore simpler than that in basic solution, and resembles

---

(3) J. L. HOARD, G. S. SMITH and M. LIND, *Advances in the Chemistry of Co-ordination Compounds* pp. 295–302, Macmillan New York, (1961).

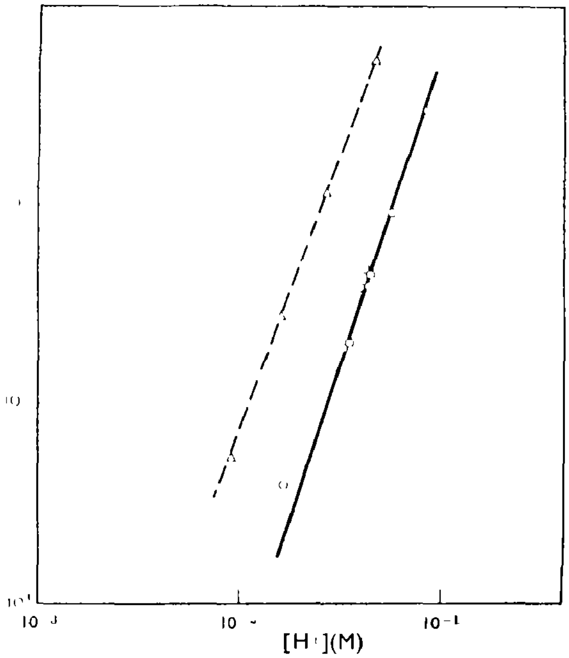


FIG. 3 — Relationship between k and $[H^+]$ in acid media 25 C, a, 1.21 × 10^{-3} M, b, 1.21 × 10^{-4} M, solid line, μ 0.20 (KNO_3), broken line, μ 0.20 (KCl)

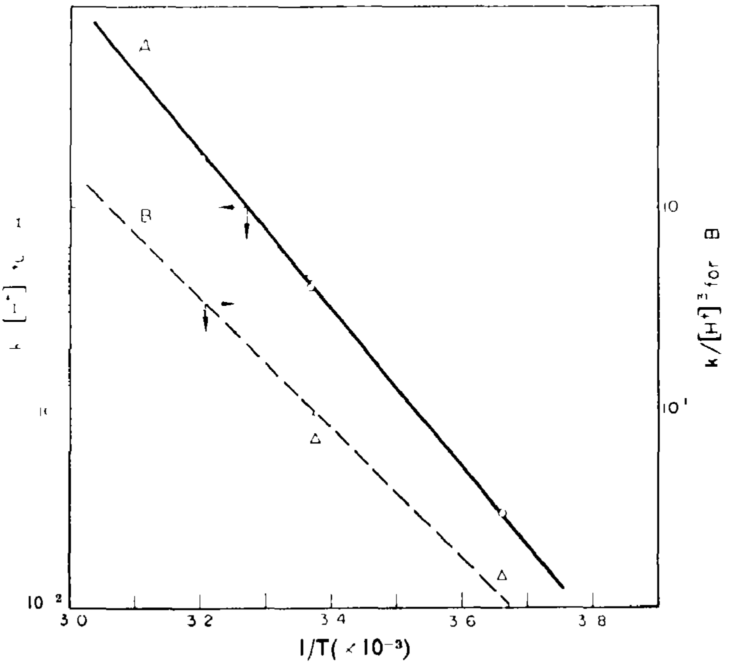


FIG. 4 — Temperature dependence of k in acid media a, 1.21 × 10^{-3} M, b, 1.21 × 10^{-4} M, solid line μ = 0.20 (KNO_3), broken line, μ = 0.20 (KCl)

TABLE 4 — RELATIONSHIP BETWEEN THE EXCHANGE RATE AND THE CONCENTRATION OF UNCOMPLEXED INDIUM AND OF INDIUM EDTA COMPLEX IN ACID MEDIA

a $(10^{-3}$ M)	b $(10^{-3}$ M)	R $(10^{-8}$ mole l^{-1} sec$^{-1})$	k $(10^{-5}$ sec$^{-1})$
0.675	1.21	4.1	3.4
0.900	1.21	4.2	3.5
1.21	1.21	4.5	3.7
1.46	1.21	4.5	3.7
1.21	0.722	4.6	3.8
1.21	1.204	3.9	3.2
1.21	1.687	4.3	3.6
1.21	2.17	4.1	3.4

$\mu = 0.20$ (KNO_3), 25°C, pH, 1.36

that of the corresponding gallium complex, the dissociation of the tri-protonated indium EDTA complex appears to be the rate-determining step. The dissociation constant of co-ordinated water is so small that the latter remains unchanged in this pH region.

$$[{}^*InY\,OH_2]^- + H^+ \rightleftarrows [{}^*InHY\,OH_2]$$

$$[{}^*InHY\,OH_2] + H^+ \rightleftarrows [{}^*InH_2Y\,OH_2]^+$$

$$[{}^*InH_2Y\,OH_2]^+ + H^+ \rightleftarrows [{}^*InH_3Y\,OH_2]^{2+}$$

$$[{}^*InH_3Y\,OH_2]^{2+} + In^{3+} \rightleftarrows [InH_3Y\,OH_2]^{2+} + {}^*In^{3+}$$

Exchange involving dissociation of the mono- or di-protonated complex is thus immeasurably slow, contrary to the case of the indium EDTA OH complex, which undergoes isotopic exchange via the monoprotonated form, the rate being given by $R = k'b[H^+]$ (4). In the species $[InH_3Y\,OH_2]^{2+}$, the In—O bonds are almost completely dissociated, and the indium EDTA complex undergoes isotopic exchange *via*

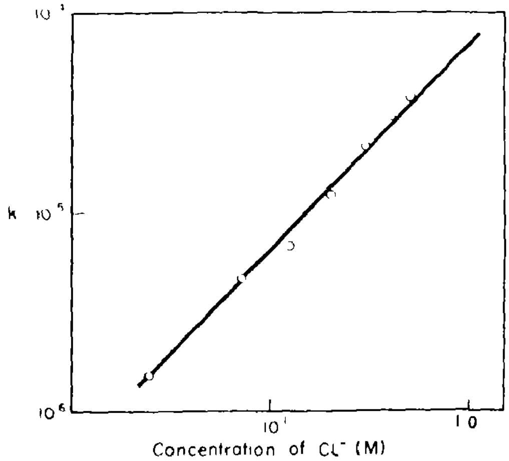


FIG. 5 — Influence of chloride ion concentration in acid media $\mu = 0.20$ (KNO_3) (except a few points with greater μ values) 25°C, pH 1.92 a, 1.21×10^{-3} M b, 1.21×10^{-3} M

dissociation of the complex, E_a is much smaller than that in weakly basic solution.

---

(4) K. SAITO and M. TSUCHIMOTO, *Bull. Chem. Soc. Japan* **35**, 367 (1962)

In solutions containing chloride ions, the co-ordinated water would be replaced by chloride ions to give $[InY\,Cl]^{2-}$,⁽²⁾ which would be protonated to give the intermediate $[InH_3Y\,Cl]^{+}$. The greater value of k' and the smaller value of E_a indicate either a greater ease of formation of this triprotonated form or a greater lability for this intermediate. Replacement of the co-ordinated water by anionic species (e.g. acetate or tartrate) increases the lability of indium EDTA-OH⁽¹⁾ but not that of the gallium EDTA or EDTA-OH complex.⁽¹⁾ Such a difference could be due to the different extent to which co-ordinated water in the indium complexes is replaced by anions.

EXPERIMENTAL

Material. ^{114}In (half-life 49 days, Radiochemical Centre, Amersham), with a specific activity ~10 μc per mg, was diluted to a specific activity of 0.41 μc per mg. The hydrated potassium salt of the indium EDTA complex, $K[InY\,H_2O]\cdot H_2O$, was prepared in crystalline form from the traced indium, commercial EDTA (acid form) and potassium hydroxide.⁽²⁾ The composition was confirmed by chemical analysis and potentiometric titration. Other chemicals were guaranteed reagents.

Kinetic runs. The procedure was the same as that for the kinetic study of the gallium complexes, except that the indium 8-quinolinol complex was precipitated at pH 3–4 with Brom-Cresol Green in ethanol as indicator. The composition of the 8-quinolinol complex was independent of the amounts of reagents in the reaction mixture. The zero-time exchange was negligible in acid solution, and ~10 per cent in basic solution. The latter can probably regarded as being separation-induced. Activity was measured by γ-ray spectrometry; β counting was more sensitive to changes in geometry and to source mounting. The weighted filter plate was wrapped with Cellotape and placed on a NaI crystal scintillator, the 1.98 MeV β-rays of ^{114m}In being absorbed by a 1 cm thick polymethyl methacrylate plate. The photomultiplier pulse was biased to produce an integrated count of the photo-electric peak of the 0.192 MeV γ-rays. The counts include those from γ-rays with high energies and the count-rate was proportional to the amount of radioactive indium.

The specific counting rate was obtained from the weight of the 8-quinolinol complex, and the fractional exchange F is given by the expression

$$F = (x_t - x_0)/(x_\infty - x_0)$$

where x_∞, x_t, and x_0 are the specific count rates at infinite time, time t and time zero, the last being about 5–30 min after mixing the solutions.

J Inorg Nucl Chem , 1963, Vol 25 pp 1253 to 1258 Pergamon Press Ltd Printed in Northern Ireland

LIGATIONAL EFFECTS IN VANADYL COMPLEXES

J SELBIN, H R MANNING* and G CESSAC*
Coates Chemical Laboratories, Louisiana State University, Baton Rouge, La

(*Received* 9 *February* 1963)

Abstract—Results of a study of the shift in the vanadium–oxygen multiple bond stretching frequency of VO(acac)$_2$ as a function of (a) solvent, (b) neutral ligand and (c) anionic ligand, are reported and discussed Ligands were found to fall into three rather distinct groups Those producing a shift of 48 ± 3 cm^{-1} include a number of primary amines, pyridine, ammonia and the moderately strong field anions NCS$^-$ and CH$_3$COO$^-$ Those producing no shift include ligands which owe much of their ligational strength to metal to ligand π-bonding, such as diphenylsulphide and triphenylphosphine, and weak field anions such as Cl$^-$, ClO$_4^-$ and NO$_3^-$ Certain ligands, such as tetrahydrofuran and *p*-dioxane, produce smaller shifts of 23 ± 1 cm^{-1} and the adducts which they form with the vanadyl complex have relatively low formation constants Frequency shifts caused by mass effects alone have no relevance in these studies

IT is now established experimentally(1) that the value of the metal oxygen multiple bond stretching frequency in metal oxycations, such as UO$_2^{2+}$ and VO^{2+}, is dependent upon the ligands attached to the oxycation entity However, there has been very little systematic investigation of this perturbation effect, particularly in regard to minimizing the number of variables inherent in such studies

MCGLYNN *et al* (1a) examined the shifts in $\bar{\nu}_3$ (the anti-symmetric stretch) of the uranyl entity in a series of six complexes K$_x$UO$_2$L$_y$(NO$_3$)$_2$, where L is the variable ligand They showed that a ligand series parallel to the "spectrochemical ligand series" may be defined using the shifts observed in $\bar{\nu}_3$ A ligand field approach was employed to rationalize the series in terms of an electrostatic contribution, as well as σ- and π-bonding contributions, to the bond strength

A similar study has been conducted with vanadyl complexes by SELBIN *et al* (1f) Vanadium–oxygen stretch frequencies for over fifty complexes of the VO^{2+} entity were recorded for a large variety of complex types and several short ligand series were derived for those cases where it was certain that a given symmetry type of vanadyl complex was being compared For example, for the symmetry type [VO(L)$_5$] the series, corresponding to decreasing $\bar{\nu}_{V-O}$, is L = H$_2$O > —NCS$^-$ > CN$^-$ > DMSO ~ F$^-$ (DMSO = dimethylsulphoxide)

NAKAMOTO *et al* (2) have reported that the $\bar{\nu}_{V-O}$ shifts from 995 cm^{-1} to 964 cm^{-1} for the complexes in the solid state upon the addition of one pyridine molecule to a molecule of $VO(acac)_2$. They also found that the addition of a pyridine molecule shifted the antisymmetric and symmetric O—U—O stretching frequencies from 915 and 838 cm^{-1} to 909 and 827 cm^{-1}, respectively, in the solid uranyl bis-(acetylacetonate) complex.

---

* National Science Foundation Undergraduate Research Participants Summer, 1962

(1a) S P MCGLYNN, J K SMITH and W C NEELY, *J Chem Phys* **35**, 105 (1961),

(1b) B SHAMBURGER Thesis, Louisiana State University, (1960),

(1c) J SELBIN, L H HOLMES, JR and S P MCGLYNN, *Chem and Industr* 746 (1961),

(1d) M E DYATKINA, V P MARKOV, I V TSAPKINA and Y N MIKHAILOV, *Zh Neorgan Khim* **6**, 575 (1961),

(1e) J SELBIN and L H HOLMES, JR , *J Inorg Nucl Chem* **24**, 1111 (1962)

(1f) J SELBIN, L H HOLMES, JR and S P MCGLYNN, *Ibid* In press

(2) K NAKAMOTO, Y MORIMOTO and A E MARTELL, *J Amer Chem Soc* **83**, 4533 (1961)

In this paper we report a study of the shift in the vanadium oxygen stretching frequency as a function of (a) solvent, (b) neutral ligand, and (c) anionic ligand, as these attach more or less strongly, to the sixth position presumed to be chemically and spatially available in the following vanadyl (IV) complexes [$VO(acac)_2$], [$VO(oxine)_2$], and [VO(en-bis-sal)] (where acac = acetylacetonate ion, oxine = 8-hydroxyquinolinate ion, and en-bis-sal = ethylenediamine-bis-salicylaldehyde). That the [$VO(acac)_2$] complex is monomeric and an example of five coordinated vanadium (IV), and that it can attach a sixth ligand has been previously demonstrated.(3)

EXPERIMENTAL

Materials

Bis-acetylacetonato-oxovanadium(IV). A reagent grade commercial product, obtained from K and K laboratories, was recrystallized twice from boiling acetone. The V-O stretch frequency of solid [$VO(acac)_2$] mulled in Nujol, occurred as a strong sharp peak at 997 cm^{-1}. Other values assigned to this vibration range from 995 to 1005 cm^{-1}. (See reference 2f for literature citations.) Found C, 45.36, H 5.44, V 18.9. Calc. for [$VO(C_5H_7O_2)_2$] C 45.29, H, 5.32, V, 19.2%.)

Bis-8-hydroxyquinolino-oxovanadium(IV). This compound was prepared by the method of Bielig and Bayer.(4a) It should be dried and stored in a vacuum desiccator, preferably in an inert atmosphere as it seems to be quite susceptible to oxidation to $VO(OH)(oxine)_2$. Found C, 60.58, H, 3.50, N, 7.65, V 14.1. Calc. for [$VO(C_9H_6NO)_2$] C, 60.79, H, 3.38, N, 7.89, V, 14.4%.)

Ethylenediamine-bis-salicylaldehydo-oxovanadium(IV). This green complex was prepared by the method of Bielig and Bayer.(4b) It was recrystallized from boiling methanol. Like the oxine complex, this one should be stored in a vacuum desiccator under nitrogen. The quadridentate ligand, ethylenediamine-bis-salicylaldehyde was prepared by slow addition of salicylaldehyde to a cooled ethylenediamine solution. The resulting yellow solid was recrystallized from a 1:1 ethanol–water or acetone-water mixture. (Found C, 57.78, H, 4.43, N, 8.32. Calc. for [$VO(C_{16}H_{14}O_2N_2)$] C, 57.66, H, 4.24, N, 8.41%.)

Other chemicals. All other chemicals used in this work were of reagent grade quality. Solvents and liquid ligands were distilled prior to use.

Spectral measurements

Infra-red spectra were recorded using a Beckman IR-7 prism-grating spectrophotometer employing NaCl optics throughout the 5000–650 cm^{-1} range. The mull technique using Nujol was used for solid samples, liquid samples were run in standard NaCl matched liquid cells. Ligand spectra were recorded separately to allow identification of ligand bands in the region of interest.

RESULTS AND DISCUSSION

That a sixth ligand attached to a [$VO(AA)_2$] complex, producing a roughly octahedral structure, can condition a significant shift of the V—O stretch frequency may be seen from the data in Table 1. (AA is either 1,10-orthophenanthroline (ophen) or α,α'-dipyridyl(dipy).) It is seen that the addition of the weak field ligands, chloride or bromide ion, to the sixth position on the vanadium (IV) produces a slight shift of $\bar{\nu}_{V-O}$ to lower frequencies. We might presumably prescribe this shift to a slight weakening of the V—O bond. However, these studies, as well as all previous studies of the metal–oxygen multiple bond stretching frequencies were carried out using solid complexes mulled in Nujol or dispersed in KBr pellets. Therefore we studied the metal-oxygen frequency shifts of vanadyl complexes dissolved in inert solvents so as to minimize any effects such as might arise from crystal packing forces and related phenomena.

---

(3) M. M. Jones, *J. Amer. Chem. Soc.* **76**, 5995 (1954), R. T. Claunch, T. W. Martin and M. M. Jones, *ibid.* **83**, 1073 (1961).

(4) (a) H. J. Bielig and E. Bayer, *Ann. Chem.* **584**, 96 (1953), (b) **580**, 135 (1953).

However, before we consider these studies, we must discuss another factor, apart from crystal forces and ligand electronic (or bonding) effects, which might be producing or at least contributing to the observed frequency shifts. This factor is the simple mass effect on vibrational frequencies. Thus we must consider the possibility that the attachment of, for example, a chloride or bromide to the vanadyl complex* is sufficient to condition the observed shift (and it certainly occurs in the predicted direction). We make the assumption that the addition of a pyridine molecule (atomic mass units = 79) to [VO(acac)$_2$] (atomic mass units of V(acac)$_2$ = 299) results in a V—O frequency shift caused *solely* by the mass effect. We can then calculate very simply† that the original frequency for [VO(acac)$_2$] of 995 cm^{-1} will be shifted to approximately 989 cm^{-1} by the attachment of a pyridine to give [VO(acac)$_2$py]. The observed shift is to 964 cm^{-1}. It thus appears that while the mass effect is significant in an absolute sense it does not contribute more than about 20 per cent to the magnitude of the observed shift. Furthermore if a series of ligands having roughly the same masses are attached to the vanadyl complex, the order of ligands, based upon the magnitude of the respective shifts should be independent of mass effects and nearly completely dependent upon ligand bonding effects. It is the latter that we are attempting to ascertain by these studies.

TABLE 1 V—O STRETCH FREQUENCIES AND EQUIVALENT CONDUCTANCES OF SELECTED VANADYL COMPLEXES

Complex	$\bar{\nu}_{V-O}$ (cm^{-1})^a	Ω^{-1} cm^{-1}^{b}
[VO(ophen)$_2$](ClO$_4$)$_2$	987	56 (3)
[VO(ophen)$_2$Cl]Cl	982	24 (2)
[VO(ophen)$_2$Br]Br H$_2$O	981	26 (2)
[VO(dipy)$_2$](ClO$_4$)$_2$	979	56 (3)
[VO(dipy)$_2$](PF$_6$)$_2$	980	–
[VO(dipy)$_2$Cl]Cl	965	18 (2)
[VO(dipy)$_2$Br]Br H$_2$O	985	25 (2)

[a] Obtained for the solid complex run in Nujol mull.

[b] Equivalent conductance obtained in nitrobenzene, number in parentheses is the number of ions indicated by the conductance value.

In seeking a suitable inert solvent in which to examine the V—O frequency shifts we obtained the data given in Table 2. The constancy of the $\bar{\nu}_{V-O}$ in several solvents is noteworthy as is the marked shift in frequency observed with the only solvent having appreciable coordinating tendencies, dimethylformamide. The vanadyl species were stable for at least an hour in all of the solvents. The solvent chosen for the remaining studies to be discussed here is chloroform.

---

* We are making the simplifying assumption here that the V—O vibration is to be considered as arising primarily from the movement (in a simple Hookian fashion) of the light oxygen with respect to the more massive vanadium plus *all* of its attached ligands.

† An alternative and more rigorous treatment than used by us of this mass effect has been carried out by S. P. McGLYNN and T. R. ORTOLANO (private communication) with the same results.

In Table 3 we have tabulated some results obtained by examining $\bar{\nu}_{V-O}$ of $[VO(acac)_2]$ in the presence of various potential ligands. The general procedure was to examine a ligand in mole ratios of vanadyl complex to ligand equal to 1:1, 1:5, and 1:25. Those ligands listed on column one of the table produced a shift of 48 ± 3 cm^{-1} when the mole ratio was 1:1. For all examples except ammonia and diethylamine (the only secondary amine studied) the original band at 1004 cm^{-1} completely disappeared for the 1:1 mole ratio. With ammonia (the molecule except for pyridine with the lowest pK value) a 1:5 mole ratio was necessary to remove the 1004 band. With diethylamine (which JONES and co-workers(3b) were able to co-ordinate to solid $[VO(acac)_2]$) the 1004 band is still present, a precipitate removes some complex from solution and the shifted band (at 954 cm^{-1}) is of weak intensity at 1:1 and medium intensity at 1:5 mole ratio. Finally, in the first column it is seen that the moderately strong field ligands NCS^- and CH_3COO^- also produce shifts of the same order of magnitude.

TABLE 2.—V—O STRETCH FREQUENCIES FOR TWO VANADYL COMPLEXES IN SELECTED SOLVENTS

Solvent	$VO(acac)_2$ $\bar{\nu}_{V-O}$ (cm^{-1})	VO(en-bis-sal) $\bar{\nu}_{V-O}$ (cm^{-1})
Nujol mull	997	990
Acetonitrile	1002	995
Chloroform	1004	990
Carbon Disulphide	1007	—
Acetone	1007	997
Nitromethane	1007	995
Benzene	1008	-
Dimethylformamide	972	-

In the third column of Table 3 are listed the ligands which produced no observable shift. These include the weak field ligands Cl^-, ClO_4^-, and NO_3^-, and those which perhaps owe their ligational strengths to metal to ligand pi bonding, such as the sulfide and phophine.

In the centre column are listed some ligands which produced shifts of 23 ± 1 cm^{-1}. For the first two the 1004 cm^{-1} band is still present and even at 1:25 mole ratios the 980 band (the shifted one) is only of medium intensity. With aniline and phenol the shifted band does not even appear until the mole ratios of 1:5 and 1:25, respectively, are examined.

Figure 1 illustrates the growth of the shifted band with increasing ligand to complex mole ratio. The ligand here is tetrahydrofuran and in IA the first and fourth bands (at 1063 and 935 cm^{-1}) are caused by this ligand. The second band (at 1028 cm^{-1}) is due to the methyl rocking vibration in the coordinated acetylacetonates, and the strongest band, the third one (at 1003 cm^{-1}) is the unperturbed V—O stretch of $[VO(acac)_2]$. In IB and IC is seen the growth in intensity of the shifted band (at 983 cm^{-1}) and the intensity decrease of the unperturbed band.

0 5 and 1 0 M acid it was found that Equation (2) is not satisfied Furthermore, as values of the partition coefficient for 0 1 M DEHPA in kerosene are greater than ten it is likely that extraction under these conditions involves formation of a polymeric uranium DEHPA complex[7] as in sulphuric acid solutions at low acidity [1]

$$UO_2X_4H_2(o) \quad UO_2^{2}(a) \quad (HX)_2(o) \rightleftarrows (UO_2)_2X_6H_2(o) \quad 2H(a) \qquad (3)$$

i e an overall reaction $2UO_2^{2}(a) \quad 3(HX)_2(o) \rightleftarrows (UO_2)_2X_6H_2(o) \quad 4H(a)$ (4)

This leads to the following relationship

$$\log 4L_1{}' \quad \log K_1 \quad 2\log(C_{\cdot} \quad 2C_1)/C_H \qquad (5)$$

where K_1 is a constant When values of $\log L_1$ were plotted vs $\log(C_{\cdot} \quad 2C_1)/C_H$ in 0 5 and 1 0 M acid it was found that Equation (5) is satisfied the slopes of the lines being 1 9 and 1 8 in 0 5 M and 1 0 M HNO_3 respectively Thus it appears that at low nitric acid concentrations uranium is extracted in accordance with Equation (4)

If we assume that at higher acidities n molecules of the DEHPA dimer combine with each uranium (VI) ion by a reaction similar to that observed with TBP viz

$$UO_2^{2}(a) \quad 2NO_3(a) \quad n(HX)_2(o) \rightleftarrows UO_2(NO_3)_2(HX)_{2n}(o) \qquad (6)$$

then the following relationship would be expected

$$\log 2^n F_1 \quad \log K_2 \quad n\log(C_{\cdot} \quad 2nC_1) \qquad (7)$$

where K_2 is a constant When the values of L_1 were plotted vs $\log(C_{\cdot} - 2nC_1)$ for values of n 1 and 2 in 6 M HNO_3 the slopes of the lines were 1 6 and 1 3 for n 1 and 2 respectively However, since either or both of reactions (1) and (3) will also occur to some extent at higher acidities the observed values of the partition coefficient are probably higher than if extraction showed a nitrate ion dependency due to Equation (6) alone As the slope of the line using $n - 1$ may therefore be greater than unity we assume that n 1 in Equation (6) i e

$$UO_2^{2}(a) \quad 2NO_3(a) \quad (HX)_2(o) \rightleftarrows UO_2(NO_3)_2(HX)_2(o) \qquad (8)$$

(b) *Dependence on uranium concentration*

When uranyl nitrate solutions containing 1 0 and 6 0 M nitric acid are extracted into 0 1 M DEHPA in kerosene at 20°C the organic phase uranium concentration was found to increase with increasing initial aqueous uranium concentration towards a limiting value (0 05 M), indicating that two molecules of DEHPA combine with each uranium ion under these conditions

(c) *Dependence on organic phase activity*

The extraction of acid from uranyl nitrate solutions (5 g/l) into 0 1 M DEHPA in kerosene was included at 20°C with the results shown in Fig 2 which also gives data for the extraction of acid in the absence of uranium

In the absence of uranium the acidity of the organic phase is approximately constant below 3 M and increases with increasing aqueous acidity above this concentration In the presence of uranium the organic phase acidity is less than in its absence

---

[7] C F Baes Jr, R A Zingaro and C F Coleman *J Phys Chem* **62**, 129 (1958)

TABLE 3.—LIGANDS WHOSE EFFECT ON THE V—O STRETCH FREQUENCY HAS BEEN STUDIED

Shift 48 ± 3 cm^{-1}	Shift 23 ± 1 cm^{-1}	No shift
Pyridine	Tetrahydrofuran[d]	Aniline (1:1)
Ammonia[a]	*p*-Dioxane[d]	Phenol (1:1)
Isobutylamine	Aniline (1:5)	Thiourea
n-Propylamine	Phenol (1:25)	Diethylether
Piperidine		Diphenylsulphide
Ethylamine		Diphenylselenide
Diethylamine[b]		Triphenylphosphine
Ethylenediamine		Triphenylarsine
KNCS[c]		Et_4NCl[e]
NH_4CH_3COO[e]		Et_4NClO_4[e]
		$AgNO_3$[d]

[a] 1004 band still present, must go to 1:5, 956 band of medium intensity

[b] 1004 band still present, ppt. removes some complex, 954 band weak at 1:1, medium at 1:5

[c] run in acetonitrile

[d] 1004 band still present, 980 band is medium at 1:25

[e] run in nitromethane

It would appear from our limited results to date that there is a maximum limit to the shift of the V—O stretch frequency, at least for the [VO(acac)$_2$] complex. We can offer no explanation of this observation at the present time. However, we can point out that all ligands producing this shift are at least moderately strong protonic bases and they generally co-ordinate well with transition metal ions. Weak field ligands or those with very weak σ-donor capacity produce little or no shift. These results find some support in the work of JONES and co-workers[3(b)] in which they found the enthalpy, entropy, and free energy of addition of ammonia and primary amines to [VO(acac)$_2$] to be relatively independent of the ligand. However we shall defer any attempts at an explanation until strong field ligands can be studied.

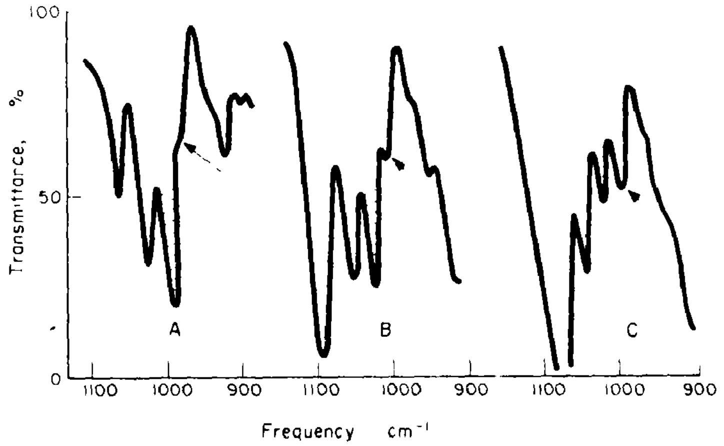


FIG. 1.—Growth of the shifted band (arrow) with increasing ligand (tetrahydrofuran) to complex mole ratio. A, 1:1, B, 5:1, C, 25:1. The shaded band is the original, unperturbed V—O stretch band of [VO(acac)$_2$] in $CHCl_3$ solvent.

Finally it is significant that with [VO(oxine)$_2$] (studied in chloroform solution) and [VO(en-bis-sal)] (studied in nitromethane solution) there was no shift observed for most of the same ligands which produced maximum shift with the acetylacetonate complex. However, with the en-bis-sal complex there was slow formation of precipitates which, when examined in nujol mulls, showed shifts up to 66 cm^{-1}. We tentatively interpret these results to indicate that the molecules of these two vanadyl complexes do not have the square pyramidal structure known from X-ray studies$^{(5)}$ for the acetylacetonate complex. Rather, it is suggested that the oxide and en-bis-sal complexes are distorted toward a trigonal bipyamidal configuration by the unsymmetrical ligands and that therefore there is no sixth position available to another ligand. Preliminary support for this postulation comes from (a) dipole moment determinations we have carried out on [VO(acac)$_2$] and [VO(oxine)$_2$], which yield values of 4.3D and 1.7D, respectively, and (b) the slow reaction of the [VO(en-bis-sal)] complex with strong ligands to produce adducts with shifted V—O stretch frequencies.

Acknowledgement—A National Science Foundation Grant (No. NSF-15242) to one of us (J. S.) is very gratefully acknowledged.

---

(5) R. P. DODGE, D. H. TEMPLETON and A. ZALKIN, *J. Chem. Phys.* 35, 55, (1961).

J Inorg Nucl Chem 1963 Vol 25, pp 1259 to 1261 Pergamon Press Ltd Printed in Northern Ireland

THE REACTION BETWEEN URANYL NITRATE AND SODIUM TRIMETAPHOSPHATE

A Indelli and G Saglietto
Chemistry Department, University of Ferrara Italy

(*Received* 1 *November* 1962, *in revised form* 3 *March* 1963)

Abstract—The precipitate formed when sodium trimetaphosphate and uranyl nitrate solutions are mixed has been identified as uranyl triphosphate by determination of uranium and phosphorous contents, by chromatographic analysis and by X-ray diffraction The reaction rate was followed by acid–base titrations and by a polarographic method The rate is dependent upon the hydrogen ion concentration, and at least two mechanisms appear to be responsible for the reaction The results may be fitted to rate equation based upon the participation of the species UO_2^{2+} and $U_2O_5H^{3}$, but more detailed analysis of the data is prevented by a lack of knowledge of the equilibria involved

When solutions of 0 1 m uranyl and trimetaphosphate ions are mixed a precipitate is formed after a few minutes Since most trimetaphosphates are easily soluble(1) it seems likely that the precipitate is a linear condensed phosphate The reaction resembles that between $Na_3P_3O_9$ and Ca^{2+} or Ba^{2+} in alkaline solution,(2) and other instances of the catalysis by metallic ions or chelates of the hydrolysis of condensed phosphates have been reported recently (3 4)

EXPERIMENTAL

Most of the chemicals were Carlo Erba" RP products, and were used without further purification Sodium salts of condensed phosphoric acids were prepared and purified as described elsewhere,(5) and conductivity water(6) was used to prepare all solutions Phosphorus was determined gravimetrically by the standard molybdate magnesium ammonium phosphate method, and also by a colorimetric method,(7) special care being taken to avoid interferences by UO_2^{2} , NO_3 and ClO_4 ions Uranium was determined colorimetrically (8) Paper chromatography was carried out by a slightly modified Ebel method (9 10) X-Ray diffraction photographs were taken with a General Electric XRD–5 set, with a copper target Potentiometric titrations in the absence of CO_2 were with a Cambridge portable pH meter and glass electrode were accurate to ~0 01 pH units (11) Polarographic measurements were made using a Sargent Polarograph, Model XII, the potential of the dropping electrode was kept at −0 88 V with respect to the mercury pool anode Under these conditions the reduction current is proportional to the UO_2^{2+} concentration, since the half-wave potential for reduction of $UO_2P_3O_{10}^{3}$ is 1 07 V with respect to S C E (12) Adequate precautions were taken to avoid contamination by O_2 and to mix the reactants only when the desired temperature had been reached

---

(1) P Pascal, *Traite de Chimie Minerale*, Masson et Cie Editeurs, Tome III, p 451, Tome VI p 621 Paris (1932)

(2) A Indelli, *Ann Chim* (Rome) **46,** 717 (1956)

(3) R Hofstetter and A E Martell, *J Amer Chem Soc* **81,** 4461 (1959)

(4) W Wieker and E Thilo, *Z Anorg Chem* **306,** 48 (1960)

(5) A Indelli, *Ann Chim* (Rome), **43,** 845 (1953) **47,** 586 (1957)

(6) A Indelli and E S Amis, *J Amer Chem Soc*, **82,** 332 (1960)

(7) C Ferrari, "*Analisi Microchimiche Colorimetriche*", p 47 C Zuffi, Bologna (1947)

(8) R G Canning and P Dixon, *Analyt Chem* **27,** 877 (1955)

(9) J P Ebel, *Bull Soc Chim France*, 991 (1953)

(10) D N Bernhart and W B Chess, *Analyt Chem* **31,** 1026 (1959)

(11) A Indelli, G Nolan, Jr and E S Amis, *J Amer Chem Soc* **82,** 3237 (1960)

(12) P R Subbaraman, N R Joshi and J Gupta, *Anal Chim Acta* **20,** 89 (1959)

RESULTS

Independently of the concentration of the reactants (0.006–0.02 M) and of the presence of $HClO_4$ (0.00–0.07 M) the precipitate had the composition U, 56.4, P, 9.4, H_2O, 10.7% (Calc for $(UO_2)_5(P_3O_{20})_2 12H_2O$ U, 57.4, P, 8.97, H_2O, 10.43%)

The solution obtained on treating the precipitate with cation exchange resin in acid form and neutralizing with NaOH contained only $Na_5P_3O_{10}$, as shown by paper chromatography. X-Ray patterns of the precipitate were complex (about fifty lines), and were similar within experimental error to the pattern of a precipitate obtained from $Na_5P_3O_{10}$ and $UO_2(NO_3)_2$ *

The acid evolved during the reaction can be titrated potentiometrically, after quenching with $Na_5P_3O_{10}$ or $Na_4P_2O_7$ to complex UO_2^{2+}. The increase in acidity and in buffer power during the reaction is clearly detectable, but quantitative data are difficult to obtain in neutral solutions because of the high rate and in acid solutions because of the small percentage increase in acidity, moreover, the buffer power of the complexing agent interferes with precise determinations. In solutions 0.0057 M in $UO_2(NO_3)_2$, 0.0023 M in $Na_3P_3O_9$ and 0.014 M in $HClO_4$ an initial rate of $d[H^+]/dt = 0.8 \times 10^{-6}$ mole l^{-1} sec^{-1} was obtained

Most of the kinetic runs were carried out polarographically, the current-time curves showed two regions, the first corresponding to the reaction

$$UO_2^{2+} + P_3O_9^{3-} + H_2O \rightarrow UO_2P_3O_{10}^{3-} + 3H^+$$

and the second (with greatly increased slope) to

$$3UO_2^{2+} + 2UO_2P_3O_{10}^{3-} \rightarrow (UO_2)_5(P_3O_{10})_2$$

From the first the initial rates reported in Table 1 were determined with an accuracy of ~5 per cent. The order with respect to H^+ ion is -0.66 when the acidity is increased from 0.00143 to 0.0143 N, beyond which the rate remains constant to 0.0714 N acid. The order with respect to UO_2^{2+} is 1.7 at $[HClO_4] = 0.00143$ (runs 1, 7 and 8) and 1.0 at $[HClO_4] = 0.0286$ (runs 5, 11 and 12). The order with respect to $P_3O_9^{3-}$ is 0.8 at $[HClO_4] = 0.0286$ (runs 5, 13 and 14). As the $P_3O_9^{3-}$ concentration is increased the rate at first increases and then decreases (runs 9, 1 and 10). From runs 1 and 15, and 5 and 16 an activation energy of 17 kcal may be calculated which is independent of the acid concentration

DISCUSSION

The analyses show the precipitate to be essentially $(UO_2)_5(P_3O_{10})_2 12H_2O$ with a slight excess of P, due probably to the adsorption of $P_3O_{10}^{5-}$ by the crystals [14]. The change in rate when $[HClO_4]$ is changed may be due to the intervention of hydrolysed species of U(VI), since the acid dissociation constant of $HP_3O_9^{2-}$ is too high[15] to be responsible for the rate decreasing towards a limiting value. The overall reaction appears to follow two paths, and the results may be explained by assuming that these

---

* A detailed list of the interplanar spacings can be obtained from the authors

[14] O T QUIMBY, *Chem Revs* **40,** 158 (1947)

[15] C W DAVIES and C B MONK, *J Chem Soc* 416 (1949)

TABLE 1.—REACTION RATES, MOLE l^{-1} SEC^{-1}, FOR THE DISAPPEARANCE OF THE URANYL ION. TEMPERATURE 25.0 C, UNLESS OTHERWISE INDICATED

n	$[UO_2(NO_3)_2]$	$[Na_3P_3O_9]$	$[HClO_4]$	$-10^6\, d[UO_2^{2+}]/dt$
1	0.00571	0.00229	0.00143	1.89
2	0.00571	0.00229	0.00286	1.29
3	0.00571	0.00229	0.00714	0.64
4	0.00571	0.00229	0.0143	0.45
5	0.00571	0.00229	0.0286	0.46
6	0.00571	0.00229	0.0714	0.46
7	0.00286	0.00229	0.00143	0.38
8	0.01143	0.00229	0.00143	3.58
9	0.00571	0.00114	0.00143	0.88
10	0.00571	0.00571	0.00143	1.35
11	0.00286	0.00229	0.0286	0.19
12	0.01143	0.00229	0.0286	0.77
13	0.00571	0.00114	0.0286	0.21
14	0.00571	0.00571	0.0286	0.72
15*	0.00571	0.00229	0.00143	7.61
16*	0.00571	0.00229	0.0286	1.77

* Temperature 40.0 C

involve the UO_2^{2+} and $U_2O_5H^{3+}$ ions. The rate would then be given by the expression

$$R = k_1 \frac{K[U(VI)]^2}{[H^+] + 4K[U(VI)]} F_1(\text{trimer}) + k_2 \frac{[H^+][U(VI)] + 2K[U(VI)]^2}{[H^+] + 4K[U(VI)]} F(\text{trimer}) \quad (1)$$

where k_1 and k_2 are the rate constants for the reactions involving the $U_2O_5H^{3+}$ and the UO_2^{2+} ions respectively, K is the equilibrium constant of the reaction

$$2UO_2^{2+} + H_2O \rightleftharpoons U_2O_5H^{3+} + H^+,$$

$[U(VI)]$ is the total uranyl concentration, F_1 (trimer) and F_2 (trimer) are functions of the $P_3O_9^{3-}$ concentration, which in runs 1 to 8 and 11 and 12 was kept constant. In deriving Equation (1) a term involving $[U_2O_5H^{3+}]^2$ has been neglected. Although this expression agrees qualitatively with the results the values of the various parameters cannot be estimated in view of the relatively poor accuracy of the data. The species $U_2O_5H^{3+}$ has not been detected previously but the formation on hydrolysis of the UO_2^{2+} ion of species containing two or more atoms of U has been repeatedly observed.(16) The dependence of the rate upon $[P_3O_9^{3-}]$ is rather puzzling although it is possible that an excess of $P_3O_9^{3}$ prevents the hydrolysis of the UO_2^{2+}. The activation energy is about the same as that for alkaline hydrolysis of $Na_3P_3O_9$ and much smaller than for acid hydrolysis.(17) It is noteworthy that the linear condensed phosphates are not appreciably hydrolysed, and the uranyl ion catalysed hydrolysis could therefore consist in a nucleophilic attack by a water molecule, assisted by the presence of a UO_2^{2+} or a $U_2O_5H^{3+}$ ion, possibly by a concerted process.(18)

---

(16) R A ROBINSON and C K LIM, *J Chem Soc* 1840 (1951), A AHRLAND S HIETANEN and L G SILLEN, *Acta Chem Scand* **8**, 1907 (1954), J A HEARNE and A G WHITE *J Chem Soc* 2168 (1951), J FAUCHERRE, *C R Acad Sci Paris* **227**, 1367 (1958), A PETERSON, *Acta Chem Scand* **15**, 101 (1961)

(17) R M HEALY and M L KILPATRICK, *J Amer Chem Soc* **77**, 5258 (1955), A INDELLI, *Ann Chim* (Rome), **46**, 367 (1956)

(18) C G SWAIN, *J Amer Chem Soc* **72**, 4578 (1950)

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 1263 to 1266. Pergamon Press Ltd. Printed in Northern Ireland

PHOTOLYSIS OF SODIUM NITROPRUSSIDE AND NITROPRUSSIC ACID

R. P. Mitra, D. V. S. Jain, A. K. Banerjee and K. V. R. Chari
Department of Chemistry, Delhi University, Delhi

(*Received* 25 *March* 1963)

Abstract—The pH of neutral solutions of sodium nitroprusside decreases on irradiation with ultra-violet light. On cutting off the light, the pH slowly rises and tends to reach its original value. If irradiation is far too prolonged, secondary reactions set in, and the pH change is no longer reversible. Titration with a base shows that irradiation under photo-reversible conditions produces a weak acid whose amount increases as irradiation proceeds, up to a maximum of two equivalents per mole of nitroprusside. The same weak acid is also produced when nitroprussic acid which, ordinarily, titrates as a strong acid, is irradiated. A mechanism of the observed changes is suggested, based on the assumption that the primary (photochemical) reaction is one of a photolysis of the nitroprusside ion, giving NO^+, which then hydrolyses to give H^+ ions.

Solutions of complex cyanides, $[M^{n+}(CN)_6]^{-(6-n)}$, where M^{n+} can be any one of Fe^{2+}, Fe^{3+}, Co^{2+}, Cr^{3+} etc., have been known to become alkaline when irradiated by ultra-violet light.(1,2) It has been suggested that photolysis of $[M^{n+}(CN)_6]^{-(6-n)}$ first takes place to give $(CN)^{-1}$ and the latter then hydrolyses, producing free alkali.

$$[M^{n+}(CN)_6]^{(6-n)-} \xrightarrow{h\nu} [M^{n+}(CN)_5]^{(5-n)-} + (CN)^{-1} \qquad (1)$$

$$(CN)^{-1} + H_2O \rightarrow HCN + OH^- \qquad (2)$$

$$[M^{n+}(CN)_5]^{(5-n)-} + H_2O \rightarrow [M^{n+}(CN)_5H_2O]^{(5-n)-} \qquad (3)$$

On cutting off the light, reactions (1, 2) and possibly also reaction (3) are reversed, giving back $[M^{n+}(CN)_6]^{(6-n)-}$ and the original pH is restored, unless irradiation has been far too prolonged.

It would be of interest to study the photolysis of complexes in which one or more $(CN)^-$ ions have been substituted by other ligands. This paper deals with the photolysis of sodium nitroprusside and nitroprussic acid. Two different structures could be envisaged for the nitroprusside ion

$$\underset{(I)}{[Fe^{2+}(CN)_5NO^+]^{2-}}, \quad \text{and} \quad \underset{(II)}{[Fe^{3+}(CN)_5NO]^{2-}}$$

The known diamagnetic character of sodium nitroprusside is strong evidence in favour of (I)(3) and our results, presented below, are also in conformity with this structure.

EXPERIMENTAL

Solutions of sodium nitroprusside were prepared in dark and kept in a refrigerator when not in use. Irradiation was done with unfiltered light from a Philips mercury discharge lamp. For measurements of pH and pH-titrations, a Beckman Zeromatic pH-meter and Beckman glass electrodes (Cat.

---

(1) S. Asperger, *Trans. Faraday Soc.* **48**, 617 (1952).
(2) A. G. MacDiarmid and N. F. Hall, *J. Amer. Chem. Soc.* **75**, 5204 (1953).
(3) L. Pauling, *J. Amer. Chem. Soc.* **53**, 3225 (1931).

No 41263) were used Nitroprussic acid was prepared by percolating solutions of sodium nitroprusside through beds of the strong acid ion-exchanger, Amberlite IR-120 (H)

RESULTS AND DISCUSSION

In sharp contrast with what has been found with the hexacyanides, the pH of solutions of sodium nitroprusside falls, instead of rising, on irradiation with U V light (curve a, Fig 1) If irradiation has not been far too prolonged, the change is photoreversible in the sense that, on cutting off the light, the pH rises and tends to re-attain its original value (curve b, Fig 1) The reversal of pH is a very much slower process than the fall in pH found during irradiation Secondary reactions set in on prolonged irradiation and the solution becomes dark blue, or even, black The pH change, then, is no longer photoreversible

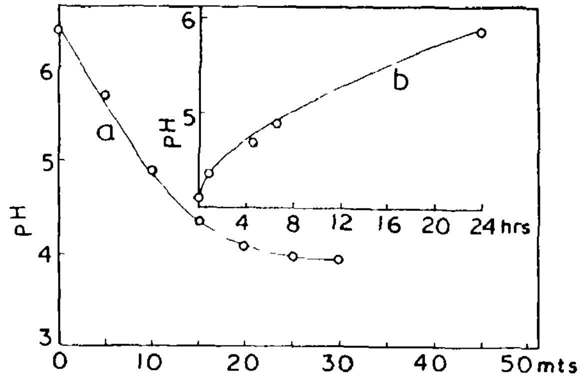


Fig 1 Effect of irradiation on the pH of solutions of sodium nitroprusside

pH-titrations (with bases) of the solutions immediately after irradiation, and before secondary reactions set in, revealed the presence of a weak acid The amount of this acid, indicated by an inflexion in the titration curve, increased with the duration of irradiation and tended to reach a limiting value which corresponded with two equivalents of alkali per mole of nitroprusside (Fig 2)

It appears that the primary reaction is one of a photolysis of the nitroprusside ion which has the structure, $[Fe^{2+}(CN)_5NO^+]^{2-}$, and gives on photolysis NO^+, the latter then hydrolyses

$$[Fe^{2+}(CN)_5NO^+]^{2-} \xrightarrow{h\nu} [Fe(CN)_5]^{3-} + NO^+ \qquad (4)$$

$$NO^+ + H_2O \longrightarrow 2H^+ + NO_2^+ \qquad (5)$$

Other reactions which then take place are the following

$$Fe(CN)_5^{3-} + H_2O \longrightarrow Fe(CN)_5H_2O^{3-} \qquad (6)$$

$$Fe(CN)_5H_2O^{3} + H^+ \rightleftharpoons \{H[Fe(CN)_5H_2O]\}^{2-} \qquad (7)$$

or,

$$[Fe(CN)_5]^{3-} + NO_2^- \longrightarrow [Fe(CN)_5NO_2]^{4-} \qquad (8)$$

$$[Fe(CN)_5NO_2]^{4} + 2H^+ \rightleftharpoons \{H_2[Fe(CN)_5NO_2]\}^{2-} \qquad (9)$$

Reaction 5 would not only explain the fall in pH observed on irradiation but would also account for the fact noted above that, in the limit, two equivalents of alkali per

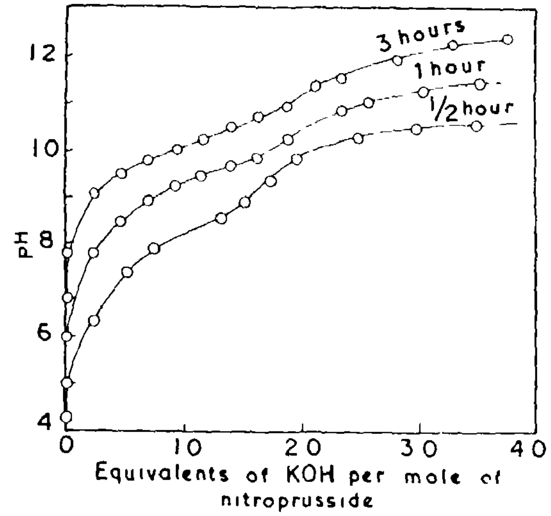


FIG. 2 pH-titration curves of irradiated solutions of sodium nitroprusside

mole of nitroprusside are used up by the (weak) acid produced as a result of irradiation Any one of the species $\{H[Fe(CN)_5H_2O]\}^{2-}$ and $\{H_2[Fe(CN)_5NO_2]\}^{2-}$ or, both of them, could be this acid

The alternative primary reactions

$$[Fe(CN)_5NO^+]^{2-} \xrightarrow{h\nu} [Fe(CN)_4NO^+]^- + CN^-, \qquad (10)$$

$$[Fe^{2+}(CN)_5NO^+]^{2-} \xrightarrow{h\nu} [Fe^{3+}(CN)_5]^{2-} + NO, \qquad (11)$$

and

$$[Fe^{3+}(CN)_5NO]^{2-} \xrightarrow{h\nu} [Fe^{3+}(CN)_5]^{2-} + NO \qquad (12)$$

are ruled out on the following grounds (a) Reaction (10) would cause a rise in pH as a result of hydrolysis of (CN) , (b) NO produced according to (11) and (12) would escape in the atmosphere as its solubility in water is very low, also, the solution containing dissolved oxygen, the NO would be oxidised to NO_2, in which case the observed photoreversibility could not be accounted for On the other hand, with reaction (4) as the primary reaction, the following mechanism would readily explain this photoreversibility

$$[Fe(CN)_5H_2O]^{3-} + NO_2^- + 2H^+ \rightarrow [Fe(CN)_5NO]^{2-} + 2H_2O \qquad (13)$$

$$[Fe(CN)_5NO_2]^{4-} + 2H^+ \rightarrow [Fe(CN)_5NO]^{2-} + H_2O \qquad (14)$$

Reactions (13) and (14) should be slow as they require several species for the formation of the transition state complex This seems to be the reason for the pH being restored very slowly after the light has been cut off

When nitroprussic acid, prepared by the ion exchange method, is irradiated with ultra-violet light, reactions similar to those taking place in the case of sodium nitroprusside, occur Only, the secondary reactions set in sooner in the acid than in the salt solution. The pH of the acid solution is already quite low (ca 2 0) and as is to be expected, no further fall in pH is observed when the weak acid, $\{H[Fe(CN)_5H_2O]\}^{2-}$ and/or $\{H_2[Fe(CN)_5NO_2]\}^{2-}$, is formed by the action of the light

That a weak acid is indeed formed as a result of irradiation is clearly seen on making pH-titrations Before irradiation, nitroprussic acid titrates as a strong acid Its pH-titration curve (a in Fig 3) has one flat segment followed by a sharp inflexion After irradiation, two segments and two inflexions appear (curve b, Fig 3) Up to the first inflexion, the (strong) nitroprussic acid is neutralised Between the first and the second inflexion, a weak acid titrates with the base The pK of this weak acid is about the same (ca 8 0) as that of the (weak) acid which is produced by the irradiation of the sodium nitroprusside solutions The acidic species appear to be the same in each case viz, $\{H[Fe(CN)_5H_2O]\}^{2-}$ and/or $\{H_2[Fe(CN)_5NO_2]\}^{2}$

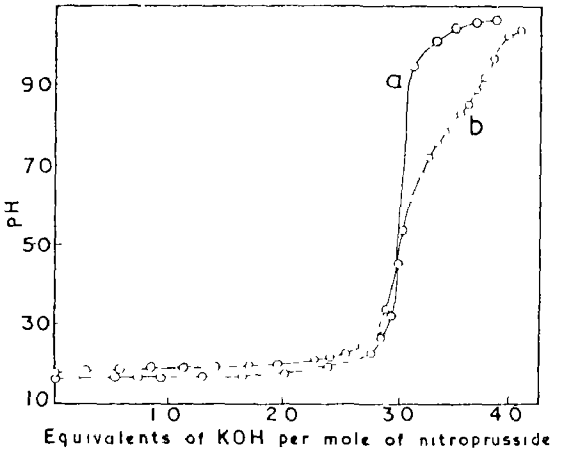


FIG 3 —pH-titration curves of nitroprussic acid before (a) and after (b) irradiation

The nature of the secondary reactions is rather uncertain and it is difficult to suggest a definite mechanism, the more so, as the instability constant of the nitroprusside ion is not known It is possible that some dissociation of the anion takes place to give Fe^{2+} ions, particularly, at the low pH of the nitroprussic acid Since nitrite ions are also present in the system some ferrous nitrites may be formed and this may be the cause of the blue black colour of the solution marking the incidence of the secondary reactions

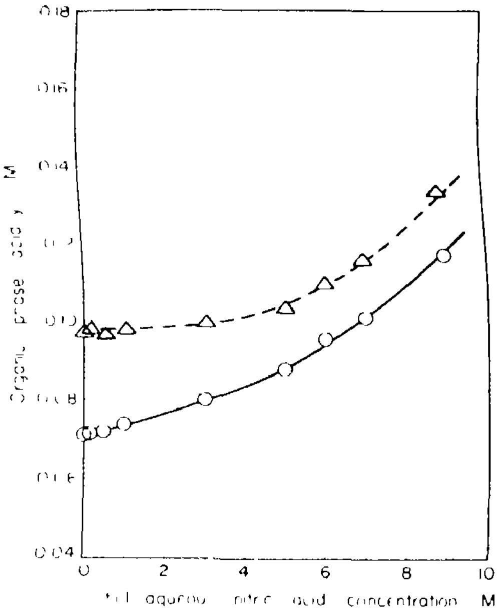


FIG. 2. Change in acidity of organic phase on extraction of uranium (VI) with 0.1 M DEHPA in kerosene (in the presence of uranium, △ in the absence of uranium)

but increases steadily with increasing aqueous acidity over the whole range. Below 3 M the change in acidity of the organic phase is analogous to that for extraction from sulphuric acid solution,[1] but at higher acidities it is presumed that nitric acid is extracted into the organic phase together with uranyl nitrate as in the case of TBP.[8]

In order to confirm this conclusion the extraction of acid from 6 M nitric acid was studied at varying DEHPA concentrations at 20°C, with the results shown in Fig. 3. The slope of the line is nearly unity (1:1), and since DEHPA is predominantly present as the dimer in the organic phase this implies that each dimeric DEHPA combines with one molecule of nitric acid by the following reaction.[9]

$$HNO_3(a) + (HX)_2(o) \rightleftarrows HNO_3(HX)_2(o) \qquad (9)$$

From Fig. 2 we may compare the change in acidity in the organic phase with the organic phase uranium concentration. In the absence of any other reaction in the organic phase two hydrogen ions are exchanged for each uranyl ion at low nitric acid concentrations, while one molecule of uranyl nitrate will displace two molecules of nitric acid extracted into the organic phase under suitable conditions at higher nitric acid concentrations. It was found that below 3 M HNO_3 change in acidity in the organic solution corresponded approximately to twice the organic phase uranium concentration, and was less than the latter at above 3 M. This confirms that DEHPA extracts uranium by an ion-exchange mechanism at low aqueous acidities, at higher acidities the extraction by DEHPA is more complicated than that with TBP,[10] since the ion-exchange reaction also occurs to some extent.

---

[8] T. SATO, *J. Inorg. Nucl. Chem.* **9**, 188 (1959).

[9] B. F. GREENFIELD and C. J. HARDY, *J. Inorg. Nucl. Chem.* **21**, 359 (1961).

[10] T. V. HEALY and H. A. C. MCKAY, *Trans. Faraday Soc.* **52**, 633 (1956).

J. Inorg. Nucl. Chem. 1963. Vol. 25. pp. 1267 to 1272. Pergamon Press Ltd. Printed in Northern Ireland

THE THERMAL DECOMPOSITION OF METAL COMPLEXES—VII

A THERMOMAGNETIC STUDY OF THE Co(III) → Co(II) REDUCTION IN COBALT(III) AMMINE COMPLEXES (1)

W. W. Wendlandt and J. P. Smith
AFOSR Centre for Molecular Research Department of Chemistry,
Texas Technological College Lubbock, Texas

(*Received* 27 *March* 1963)

Abstract—The Co(III) → Co(II) reduction reaction was studied by means of a high temperature Gouy magnetic susceptibility apparatus for the complexes $[Co(NH_3)_6]X_3$ (X = Cl, Br, I and NO_3), $[Co(NH_3)_6]_2(SO_4)_3 \cdot 2.5H_2O$, $[Co(NH_3)_5H_2O]X_3$ (X = Cl, Br, I, and NO_3), $[Co(NH_3)_5X]X_2$ (X = Cl, Br, I, and NO_3), and $[Co(NH_3)_5X]Y_2$ (X and Y may be Cl, Br and I). Minimum reduction temperatures were in the 100–200° temperature range with most of them in the 150–200° range. The curves for $[Co(NH_3)_5Br]I_2$ and $[Co(NH_3)_5Cl]I_2$ had a pronounced break at 193 and 185°, respectively. Two possible reduction mechanisms are indicated for these two complexes.

The thermal dissociation of a number of cobalt (III) ammine complexes has previously been studied in this Laboratory. Thermogravimetric analysis (TGA), differential thermal analysis (DTA), gas evolution analysis (GE), and the stoicheiometry for the thermal dissociation of $[Co(NH_3)_6]X_3$ (where X = Cl, Br, I, and NO_3),(2) $[Co(NH_3)_6]_2(SO_4)_3$,(2) $[Co(NH_3)_5X]Y_2$ (where X and Y may be Cl, Br, and I),(3) and $[Co(NH_3)_5H_2O]X_3$ (where X = Cl, Br, I, and NO_3)(4) have previously been reported.

The terminal cobalt compound in all of these studies was either the cobalt (II) halide or sulphate or cobalt (II, III) oxide, Co_3O_4. Since the initial complexes contained cobalt (III), it is obvious that a reduction of the cobalt ion took place during the thermal dissociation reaction. The nature of this reduction step is not very well understood. It has been shown that the reducing agent can be either co-ordinated ammonia or co-ordinated or ionic iodide ion. For complexes containing ammonia, but no iodide or nitrate ions, the dissociation stoicheiometry is (2)

$$6[Co(NH_3)_6]X_3(s) \xrightarrow{He} 6CoX_2(s) + N_2(g) + 6NH_4X(s) + 28NH_3(g)$$

Likewise, for $[Co(NH_3)_5X]Y_2$ compounds not containing iodide, the reaction is similar to that above, or (3)

$$6[Co(NH_3)_5X]Y_2(s) \xrightarrow{He} 6CoY_2(s) + 6NH_4X(s) + 22NH_3(g) + N_2(g)$$

However, for iodide containing complexes, $[Co(NH_3)_5X]I_2$, the reaction is (3)

$$2[Co(NH_3)_5X]I_2(s) \xrightarrow{He} CoX_2(s) + CoI_2(s) + I_2(g) + 10NH_3(g)$$

The reducing agent for those compounds containing both ammonia and an oxidizing group such as the nitrate ion is not known. These complexes explode when heated and the resulting reaction must be more complicated than for those complexes containing only halide or sulphate ions

---

(1) For Part (VI) see W. W. Wendlandt and J. P. Smith *J. Inorg. Nucl. Chem.* **25**, 833 (1963).

(2) W. W. Wendlandt, *J. Inorg. Nucl. Chem.* **25**, 545 (1963).

(3) W. W. Wendlandt and J. P. Smith, *J. Inorg. Nucl. Chem.* In press.

(4) W. W. Wendlandt and T. L. Bear, *J. Phys. Chem.* **65**, 1516 (1961).

The cobalt (III) ammines are diamagnetic due to a d^6 electron configuration in a spin-paired d^2sp^3 octahedral structure (5) On reduction from Co(III) → Co(II), the cobalt (II) ion has a d^7 configuration with three unpaired electrons so that it is paramagnetic (6) Thus, it should be possible to study the reduction of the Co(III) ion in the complexes by measuring the magnetic properties of the compounds as a function of temperature In this manner, the reduction reaction may be observed even though there are other simultaneously occurring reactions such as loss of ammonia, sublimation reactions, and so on

EXPERIMENTAL

Preparation of complexes The complexes studied were the same compounds that were used for the previous investigations(2 4) except for the aquopentammine-complexes These were prepared according to previous methods (7 9)

High temperature magnetic susceptibility apparatus A high temperature Gouy magnetic susceptibility apparatus was employed which consisted of an automatic recording Sartorius single pan balance, Model No 2503, an Atomic Laboratories aluminium foil-wound electromagnet, and a suitable d c power supply The recording balance output was recorded on a Westronics 0-5 mV strip-chart potentiometric recorder whose full scale span corresponded to a 10 mg sample weight change The sample was sealed into an evacuated glass tube, 5 mm in diameter by 34 cm in length, and suspended by a platinum wire from the balance pan The furnace consisted of a Pyrex glass tube, 2 0 cm in diameter by 15 cm in length, wound with enough Nichrome resistance wire to give a total resistance of about 15 Ω The entire assembly was well insulated with asbestos paper to protect the magnet pole faces The furnace power supply has been previously described (10) The temperature of the furnace was measured by a chromel-alumel thermocouple located in the centre of the furnace near the glass sample tube The thermocouple output was recorded on another Westronics strip-chart potentiometric recorder whose chart paper drive was synchronous with the balance recorder

The procedure for a run consisted of the following About 70–80 mg of sample was mixed with 70-80 mg of previously ignited aluminium oxide and placed into the sample tube The purpose of the alumina was to prevent any drastic changes of sample density due to the fusion of the sample or sample decomposition products The sample tube was then evacuated to ~1 mm, sealed off at the top, and suspended in the furnace After adjusting the magnetic field to about 8,000 Gs, the heating cycle of the furnace was begun and the change in weight of the sample recorded The usual weight change of the sample during heating was 8–10 mg A heating rate of about 5 C per min was employed from ambient to 500 C At least duplicate runs were made on each compound

No attempts were made to calculate the specific or molar magnetic susceptibilities for each of the complexes since it was the change in magnetic susceptibilities for each of the complexes with temperature which was desired Besides, due to the small density changes caused by the thermal dissociation process, it would not have been possible to calculate these quantities for the products

RESULTS AND DISCUSSION

The thermomagnetic curves of the complexes are given in Figs 1–4

The change in the magnetic susceptibility of $[Co(NH_3)_6]X_3$ (X = Cl, Br, I, and NO_3)

---

(5) R W ASMUSSEN, "Magnetokemiske Undersøgelser over Uorganiske Kompleksforbindelser", Gjellerup Forlag, Copenhagen, 1944

(6) B M FIGGIS and J LEWIS, *Modern Co-ordination Chemistry* (Edited by J LEWIS and R G WILKENS) Chap 6 Interscience, New York (1960)

(7) A KING, "*Inorganic Preparations*", pp 103 and 106 Van Nostrand, New York (1936)

(8) H DIEHL, H CLARK and H H WILLARD, *Inorganic Syntheses* (Edited by H S BOOTH) Vol 1, p 186 McGraw-Hill, New York (1939)

(9) F BASOLO and R K MURMANN, *Inorganic Syntheses* (Edited by J C BAILAR) Vol 4, p 174 McGraw-Hill, New York (1953)

(10) W W WENDLANDT, *J Chem Educ* **38**, 571 (1961)

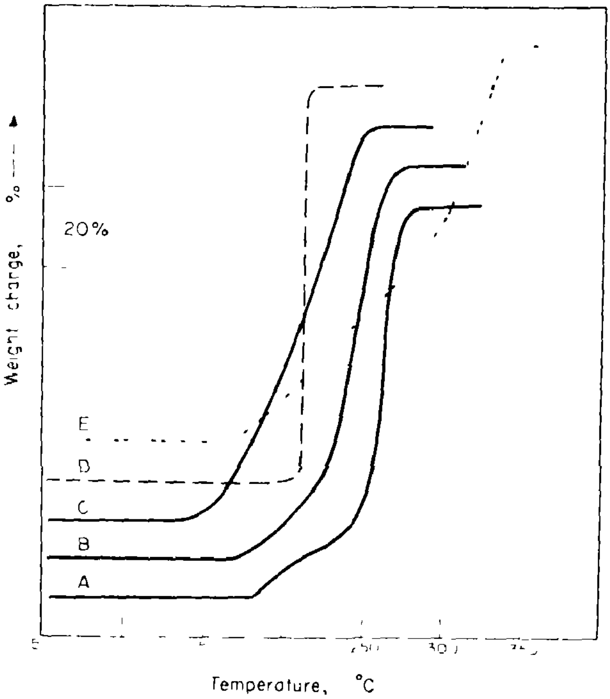


Fig. 1 — Thermomagnetic curves of cobalt (III) complexes
A $[Co(NH_3)_6]Cl_3$, *B* $[Co(NH_3)_6]Br_3$ *C* $[Co(NH_3)_6]I_3$ *D* $[Co(NH_3)_6](NO_3)_3$
E $[Co(NH_3)_6]_2(SO_4)_3$ 2 $5H_2O$

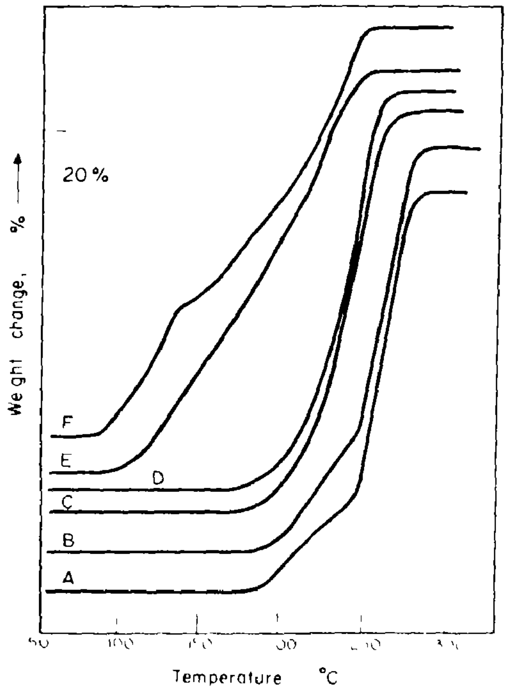


Fig. 2 — Thermomagnetic curves of cobalt (III) complexes
A $[Co(NH_3)_5Cl]Cl_2$, *B* $[Co(NH_3)_5H_2O]Cl_3$, *C* $[Co(NH_3)_5Br]Br_2$
D $[Co(NH_3)_5H_2O]Br_3$, *E* $[Co(NH_3)_5I]I_2$, *F* $[Co(NH_3)_5H_2O]I_3$

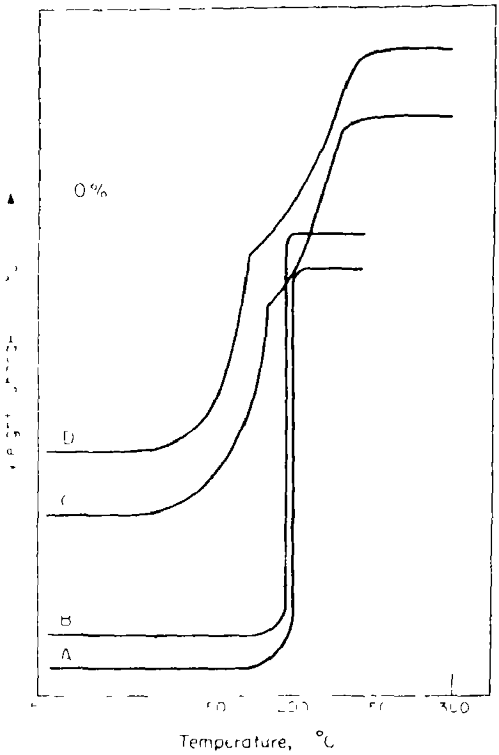


FIG. 3 Thermomagnetic curves of cobalt (III) complexes
A $[Co(NH_3)_5H_2O](NO_3)_3$, *B* $[Co(NH_3)_5NO_3](NO_3)_2$, *C* $[Co(NH_3)_5Br]I_2$, *D* $[Co(NH_3)_5Cl]I_2$

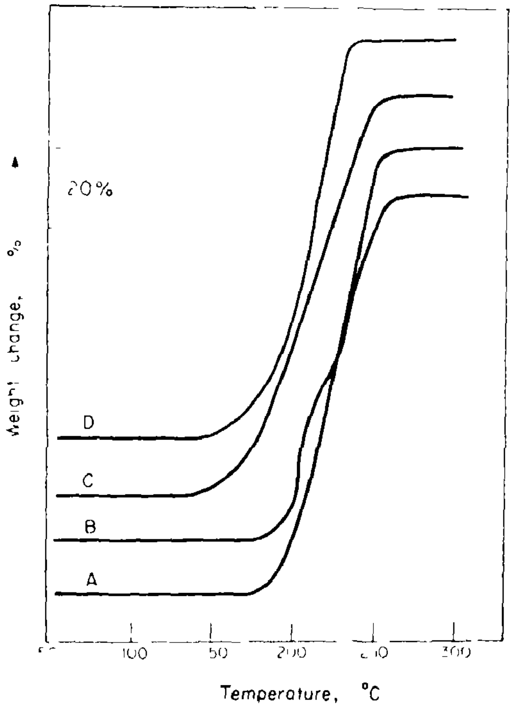


FIG. 4 —Thermomagnetic curves of cobalt (III) complexes
A $[Co(NH_3)_5Cl]Br_2$, *B* $[Co(NH_3)_5Br]Cl_2$, *C* $[Co(NH_3)_5I]Br_2$, *D* $[Co(NH_3)_5I]Cl_2$

and $[Co(NH_3)_6]_2(SO_4)_3 \cdot 2.5H_2O$ with temperature is given in Fig. 1. Except for $[Co(NH_3)_6](NO_3)_3$, the reduction reaction, $Co(III) \rightarrow Co(II)$, was a rather gradual one. In fact, if the curves are inverted, they look similar to the thermobalance weight-loss curves obtained for these complexes. The nitrate complex, due to the explosive nature of the dissociation reaction, showed an abrupt change from diamagnetic to paramagnetic character.

The curve for $[Co(NH_3)_6]Cl_3$ indicated that the reduction of the Co(III) ion began at about 173°, somewhat lower than the temperature at which thermal dissociation began as determined by DTA studies.(2) However, this difference may be due to the differences in sample heating rates or to the nature of the sample holder itself. The minimum reduction temperature is also lower than the thermal dissociation temperatures reported in an ammonia atmosphere.(11) According to the latter report, the dissociation of the chloride proceeds through an intermediate, $[Co(NH_3)_5Cl]Cl_2$. On further heating to 250°, it decomposes to give $CoCl_2$, N_2, NH_4Cl and NH_3. It is seen that this intermediate is not formed under the conditions of this experiment since $[Co(NH_3)_5Cl]Cl_2$ should also be diamagnetic. From the curve it is seen that the reduction reaction may possibly take place through two steps. The first step, from 173 to 250°, is a slow one followed by a very rapid reduction from 250 to about 285°.

The thermomagnetic curve for $[Co(NH_3)_6]Br_3$ was similar to that of the chloride, except that the reduction of the Co(III) began at about 168° and was completed at 278°. At 278°, the sample was a dark blue colour which turned to green on further heating to 400°. The latter green compound is probably $CoBr_2$. Similarly, the curve for $[Co(NH_3)_6]I_3$ indicated a gradual reduction reaction from 140 to 255°. The curve for $[Co(NH_3)_6]_2(SO_4)_3 \cdot 2.5H_2O$ showed that reduction began at about 166° and was completed at 345°. The first step in the reduction curve was somewhat longer than was found for the chloride or bromide complexes.

The thermomagnetic curve for $[Co(NH_3)_6](NO_3)_3$ showed that the reduction reaction began at about 190°. It became very rapid at 215° and was completed at about 220°. This is in fairly good agreement with the DTA curve for the thermal dissociation reaction.(2)

The change in magnetic susceptibility for the $[Co(NH_3)_5H_2O]X_3$ (X = Cl, Br, I, and NO_3) and $[Co(NH_3)_5X]X_2$ (X = Cl, Br, I, and NO_3) type complexes are given in Figs. 2 and 3. There should be little difference between the curves for the aquopentammine- and the anionopentammine-complexes for a given anion because the anionopentammine-complex is first formed by the deaquation reaction

$$[Co(NH_3)_5H_2O]X_3 \rightarrow [Co(NH_3)_5X]X_2 + H_2O$$

This was indeed found to be the case. The minimum reduction temperatures were $[Co(NH_3)_5H_2O]Cl_3$, 178°, $[Co(NH_3)_5Cl]Cl_2$, 175°, $[Co(NH_3)_5H_2O]Br_3$, 162°, $[Co(NH_3)_5Br]Br_2$, 167°, $[Co(NH_3)_5H_2O]I_3$, 84°, $[Co(NH_3)_5I]I_2$, 83°, $[Co(NH_3)_5H_2O](NO_3)_3$, 187°, $[Co(NH_3)_5(NO_3)](NO_3)_2$, 185°. Except for the iodide complexes the minimum reduction temperatures were similar to those found for the $[Co(NH_3)_6]X_3$ series of complexes.

The magnetic susceptibility curves for $[Co(NH_3)_5H_2O]Cl_3$ and $[Co(NH_3)_5Cl]Cl_2$ again showed a possible two step reduction of the Co(III) ion as was indicated for

---

(11) W. Biltz, *Z. Anorg. Chem.* **83**, 177 (1913).

$[Co(NH_3)_6]Cl_3$. This two step reduction was not so evident from the bromide curves.

The remaining magnetic curves for the anionopentammine-complexes are given in Figs. 3 and 4. These complexes were of the general formula, $[Co(NH_3)_5X]Y_2$, in which X and Y may be Cl, Br, and I.

The curves for $[Co(NH_3)_5Cl]Br_2$ and $[Co(NH_3)_5Br]Cl_2$ were similar to those found for the corresponding anionopentammine complexes in which the anions in both the ionization and co-ordination spheres were identical. For all of those complexes containing iodide, either in the co-ordination or ionization spheres, the reduction reaction began at a much lower temperature than for those not containing this ion. This confirms the fact that the reducing agent in these complexes is the iodide ion. In all cases, the vapor of free iodine was visible in the sealed tubes.

The minimum reduction temperatures for these complexes were: $[Co(NH_3)_5X]Y_2$ where X and Y are Cl]Br_2, 175°, Br]Cl_2, 177°, Br]I_2, 119°, Cl]I_2, 115°, I]Br_2, 130°, and I]Cl_2, 135°.

The curves for $[Co(NH_3)_5Br]I_2$ and $[Co(NH_3)_5Cl]I_2$ were similar in that both had a pronounced break at 193 and 185°, respectively. These breaks came at about 50 and 53 per cent respectively, of the total weight change for the complete reduction of Co(III) → Co(II). This would appear to indicate that the reduction was carried out in two steps by two different mechanisms, i.e., by iodide ion or by ammonia. Qualitatively, from the iodide vapour in the tubes at the lower temperatures, it was thought that the iodide ion was the reducing agent for the first step. Thermal decomposition of a sample of $[Co(NH_3)_5Br]I_2$, minus the Al_2O_3, under the same conditions as in the magnetic balance, gave a residue which corresponded closely to the composition, $CoBrI_{1.5}(NH_3)_{1.51}\frac{1}{8}I_2$. It seems probable that in the first step, the reduction is brought about by the iodide ion while in the second step, the reduction is by iodide ion as well as ammonia. The same type of intermediate compound is possible for $[Co(NH_3)_5Cl]I_2$ although it was not isolated.

The curves for $[Co(NH_3)_5I]Cl_2$ and $[Co(NH_3)_5I]Br_2$ showed continuous reduction from 130°–135° to 238–257°.

Acknowledgement.—This work was supported by the U.S. Air Force Office of Scientific Research through Grant No. AF-AFOSR-23-63. The loan of the electromagnet from DR. R. J. THOMPSON is gratefully acknowledged.

J Inorg Nucl Chem 1963 Vol 25, pp 1273 to 1286 Pergamon Press Ltd Printed in Northern Ireland

THE EXTRACTION OF LANTHANONS WITH ALKALI METAL AMALGAMS—III

STUDIES OF MODEL SYSTEMS

M F BARRETT, D SWEASEY and N E TOPP
National Chemical Laboratories Teddington, Middlesex, England

(*Received* 8 *March* 1963)

Abstract—The extraction of the lanthanon elements with alkali amalgams has been examined Seven of the lanthanon elements extract, and different efficiency sequences are found The La–Nd group are extracted in the sequence Li Na K, while the Sm–Eu–Yb group extract in the order Na K Li Divalent ions are formed during the extraction of the last three elements, and, when extracted from binary mixtures, these elements are enriched in the amalgam phase

The e m f of a number of lanthan amalgam cells have been measured They are all lower that the e m f of the corresponding alkali amalgam cells It is suggested that extraction is the sum of two opposing effects, electrochemical and hydrolytic The evidence suggests that the La–Nd group are reduced by a three-electron reduction, while the Sm–Eu Yb group are first reduced to the divalent state

IN AN earlier paper, the extraction of aqueous solutions of some complex rare earth fractions with sodium amalgam was studied[1] It was shown that samarium and ytterbium could be extracted in a reproducible manner by a simple batch extraction procedure The important variables controlling the efficiency of the extraction process were the samarium or ytterbium content of the lanthanon fraction and the acidity of the solution It was concluded that the extraction must be an electrochemical process, although direct evidence for this was not obtained The systems studied were too complex to throw much light on the mechanism of the extraction process

Further work has been carried out using carefully purified rare earth materials Extraction experiments have been performed on the individual rare earths and on simple binary model systems Polarography of the rare earth elements has been re-examined and electrochemical measurements have been made on a number of amalgam systems by static and kinetic methods

This work has established that seven of the rare earth elements are extracted by alkali amalgams The reduction is electrochemical, and it is suggested that it is due to the sum of two opposing effects, electrochemical and hydrolytic The La–Nd elements appear to reduce by a three-electron reduction, while Sm Eu and Yb are reduced to the divalent state before reduction to the metal

EXPERIMENTAL

Materials All of the rare earth oxides used were of 99 9 per cent purity With the exception of cerium and europium, they were isolated by ion-exchange chromatography Cerous salts were prepared from A R ceric ammonium nitrate This was reduced to the Ce^{3} state with a small excess of hydroxylamine and precipitated with ammonium carbonate

---

[1] M F BARRETT, D SWEASEY and N E TOPP, *J Inorg Nucl Chem* **24**, 571 (1962)

Europium was purified by the reduction and precipitation procedure of McCoy.[2,3] Neutral acetate stock solutions of the rare earth materials were prepared. (Approx. 1 N.) All reagents used were of A.R. quality.

Preparation of amalgams. Sodium and potassium amalgams were prepared by direct addition, as described in Part I. This method was unsuitable for the preparation of lithium amalgam, so it was prepared by the electrolysis of the hydroxide using a mercury cathode. Alkali metal amalgams were washed and standardized by methods described previously.

Two methods were used for preparing rare earth amalgams. Amalgams of the elements listed in Table 2 could be prepared by extraction with a suitable alkali metal amalgam. The products usually contained a small residue of alkali metal which was removed by washing with alcoholic acetic acid. The e.m.f. of the amalgam cell was a useful criterion of purity.

A more general method was to heat mercury and metal (obtained from Johnson Matthey) together in an evacuated Carius tube. The reaction time varied with the metal. Light earth metals reacted completely in 6 hr at 500°C but up to 48 hr was required by some of the heavy earths. There was no evidence of attack on the glass.

Analytical methods. Spectroscopic and spectrophotometric methods for the analysis of the rare earth elements were described in Part I. Sodium determinations were carried out by flame photometry, using a Beckman instrument. The estimation of zinc, and the polarographic behaviour of the rare earth elements were examined with a Cambridge polarograph (Type T. G. 2) fitted with the Univector device.

Extraction procedure. The extraction experiments were carried out in a U-tube apparatus of the type described in Part I. A packed column was used in all cases. The amalgams were discharged through a 1 mm diameter capillary at a flow-rate of 100 gs/min. The lanthanon material balance was established gravimetrically, using oxalate precipitation.

In some experiments, the hydrogen evolved during extraction was estimated. For this purpose, the extraction column was provided with a cone and socket joint holding a gas exit tube as well as the capillary used for supplying sodium amalgam. The hydrogen was passed through a cold trap (CO_2–acetone) and then over heated copper oxide, the water was collected in magnesium perchlorate and weighed. The apparatus was calibrated by reacting a standard quantity of sodium amalgam with 1 N hydrochloric acid.

Electrochemical techniques. A small cell was constructed with a vertical capillary (1 mm bore) which supported an amalgam drop acting as the cathode. Fresh amalgam was supplied to this from a reservoir, the amalgam surface in the reservoir being protected with a layer of dry alcohol. The electrolyte was purged with argon. To prevent creep of the electrolyte, the capillary was treated internally with a silicone. The cell was completed with a saturated calomel electrode. Measurements on static systems were made with a Pye potentiometer and galvanometer.

For measurements with kinetic systems, the amalgam feed was modified by incorporating a syringe, which made it possible to form fresh drops of sodium amalgam on the cathode of reproducible size (Fig. 1). The change of e.m.f. with time was followed with a Solartron oscilloscope. The final e.m.f. could be measured potentiometrically.

THE EXTRACTION OF LANTHANONS WITH AMALGAMS

1. *Stoicheiometry of the extraction process*

In Part I, it was suggested that the extraction of lanthanons took place by the reaction

$$Ln^{3+} + 3Na \rightarrow Ln + 3Na^{+} \qquad (1)$$

or

$$Ln^{3+} \xrightarrow{Na} Ln^{2+} + Na^{+} \xrightarrow{2Na} Ln + 3Na^{+} \qquad (2)$$

and that some sodium reacted with hydrogen ions in solution

$$2Na + 2H^{+} \rightarrow 2Na^{+} + H_2 \qquad (3)$$

---

(2) H. N. McCoy, *J. Amer. Chem. Soc.* **57**, 1756 (1935).

(3) H. N. McCoy, *J. Amer. Chem. Soc.* **58**, 2279 (1936).

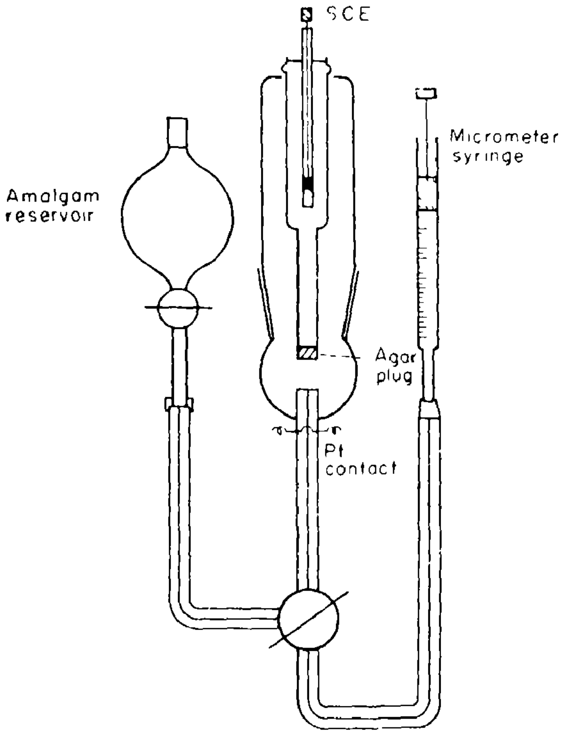


FIG. 1 — Amalgam electrode cell

It was found that lanthanon amalgams were stripped by passage through a column of hot hydrochloric acid (~80°C, 4 N).⁽¹⁾ By using the method described above, the hydrogen evolved during stripping was determined and compared with the lanthanon found in the extraction column (Table 1, columns 2 and 3). The two were in excellent agreement, showing that lanthanons are reduced to the metal in the extraction step.

Material balance during extraction was obtained in a similar way by comparing the sodium consumption with evolved hydrogen and extracted lanthanon. A small amount of sodium was found in the lanthanum amalgam (2–3 per cent) and the result in Table 1 has been corrected for this. In all cases, good agreement was obtained between sodium consumption, and the sum of evolved hydrogen and extracted lanthanon (Columns 6 and 7).

TABLE 1.—STOICHIOMETRY OF EXTRACTION PROCESS

Lanthanon	Amalgam stripping		Extraction experiments			
	Extracted Ln_2O_3(mg-eq.)	Evolved H_2 (mg-eq.)	Extracted Ln_2O_3(mg-eq.)	Evolved H_2 (mg-eq.)	(Ln_2O_3 + H_2) (mg-eq.)	Added Na (mg-eq.)
Sm	3.15	3.13	22.35	7.06	29.4	30.3
Yb	2.92	2.94	14.95	16.04	31.0	30.3
La	2.98	2.95	4.65	14.55	19.2	19.1

It will be clear that such a method cannot differentiate side reactions such as $2Ln^{2+} + 2H^+ \rightarrow 2L^{3+} + H_2$ or $2Ln + 6H^+ \rightarrow 2Ln^{3+} + 3H_2$ from $2Na + 2H^+ \rightarrow 2Na^+ + H_2$.

⁽¹⁾ M. F. BARRETT and N. E. TODD, *J. Appl. Chem.* 13, 7 (1963).

II *The extraction of lanthanons with sodium amalgam*

From stock solutions 0·5 N solutions of the lanthanon acetates, containing 0·5 N acetic acid, were prepared. The pH of the solutions was about 4·0. Fifty-ml portions of these solutions were extracted with a dilute (0·1% w/w) sodium amalgam, using the method described in Part I. The extraction curves are shown in Fig. 2.

The amalgams of Sm, Eu and Yb are less stable than the other rare earth amalgams, and the amount extracted depended on the contact time of amalgam and solution.

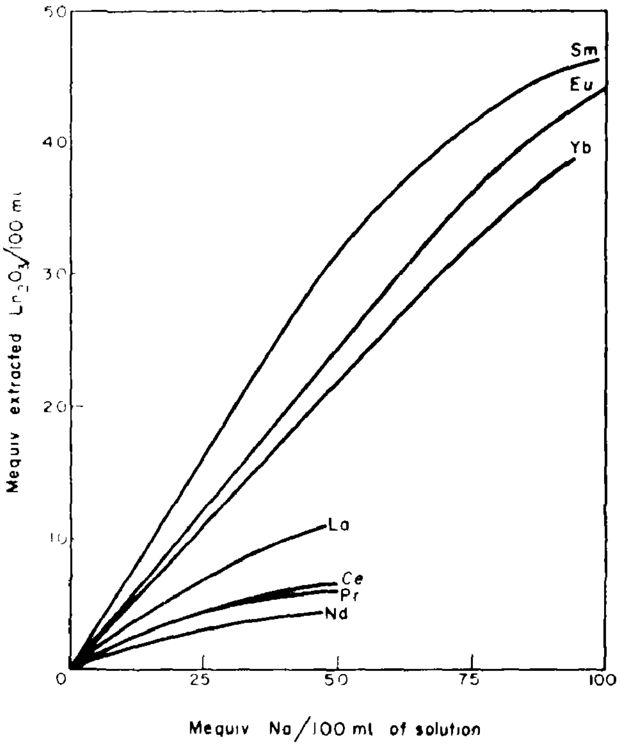


FIG. 2.—Extraction of lanthanons with sodium amalgam.

Prolonged extraction caused a depletion of these amalgams by a back-extraction with hydrogen ions (Part I). The other amalgams are more resistant to acidic attack, and essentially similar extraction curves were obtained with 50, 100 and 150 ml volumes of lanthanum acetate.

Seven of the lanthanon elements were extracted, forming two groups. In the lanthanum–neodymium group, the extraction efficiency (equivalents lanthanon extracted per equivalent of alkali) decreased in a regular sequence. It also decreased during the progress of extraction. With lanthanum, about 20 per cent of the material initially in solution was extracted, decreasing to 7 per cent with neodymium. In each case, one extraction was continued until just short of precipitation of the lanthanon hydroxide. The pH of the extracted solution was above 6·0 in such cases. No colour changes were observed during extraction.

The three elements samarium, europium and ytterbium were extracted at a much higher efficiency. This was constant for the greater part of the extraction, but decreased after about 80 per cent of the elements had been extracted from solution. The

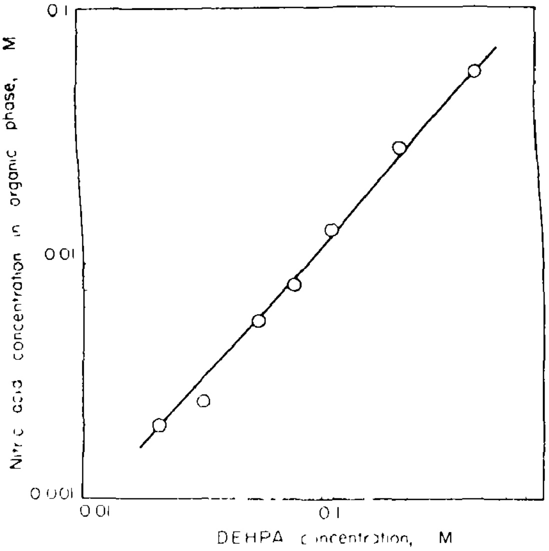


FIG 3 —Variation of nitric acid in organic phase with DEHPA concentration on extraction of 6 0 M nitric acid solution by DEHPA in kerosene in the absence of uranium

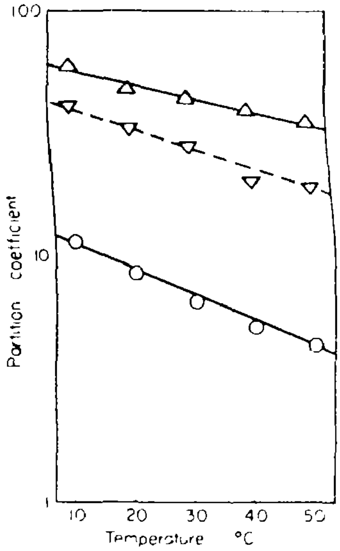


FIG 4 Variation of partition coefficient with temperature on extraction of uranium (VI) from nitric acid solutions by 0 1 M DEHPA in kerosene (and ○, at 0 5 and 6 0 M nitric acid concentrations respectively) or 19 % TBP in kerosene (▽ at 6 0 M nitric acid concentration) $UO_2(NO_3)_2$5g/l

(d) *Temperature effects*

Fig 4 which includes data for 19 % TBP in kerosene[11] for comparison, shows that although the partition coefficient decreases with increasing temperature, the variation in 6 M acid is greater than that in 0 5 M acid The heat of reaction (change in enthalpy) in equation (1) or (8) was estimated from these data to be 2 46 kcal/mole in 0 5 M HNO_3 and 4 72 kcal/mole in 6 M HNO_3 The heat of the reaction[12]

$$UO_2^{2+}(a) + 2NO_3^-(a) + 2TBP(o) \rightleftarrows UO_2(NO_3)_2\,2TBP(o) \qquad (10)$$

was found to be 3 69 kcal/mole in 6 M HNO_3 The heat of reaction for the extraction of uranium by DEHPA at higher nitric acid concentrations is therefore close to that for TBP, but is larger than that for DEHPA at low acidities

(e) *Infra-red spectra*

Organic phases were examined from the extractions of uranyl nitrate solutions (5 and 25 g/l) at different acidities into 0 1 M DEHPA in kerosene at 20°C Similar experiments were carried out in the absence of uranium Data for the higher concentration of uranyl nitrate are presented in Fig 5

Spectra of DEHPA in kerosene show the P→O frequency at 1230 cm^{-1} OH stretching bands at 2680 and 2350 cm^{-1}, which are attributed to the formation of dimer, and the OH bending band at 1690 cm^{-1} Although the spectra from 0 15 and 1 0 M extraction efficiency again decreased in the atomic number sequence. Quantitatively, extraction was incomplete, although more than 90 per cent of each element was extracted. Colour changes were observed during the extraction. With samarium, a faint red colour appeared which disappeared immediately the flow of amalgam was stopped. Europium gave a pale yellow colour, and ytterbium a bright orange; these colours persisted for several minutes after stopping the amalgam flow. Formation of the Eu^{2+} ion was proved by comparing the absorption spectrum of a typical extract solution with an authentic Eu^{2+} solution prepared with a Jones reductor (3, *loc. cit.*). The formation of Yb^{2+} during extraction has already been proved (Part I). It is probable that the Sm^{2+} ion was formed during the extraction of samarium, but its extreme instability made a simple proof impossible.

---

[11] T SATO, *J Inorg Nucl Chem* **6**, 334 (1958)

[12] R I MOORE U S A E C Report, AECD-3196 (1951)

None of the other lanthanon elements, or yttrium, was extracted. The detection limit was 1 mg or 0·05 per cent of the lanthanon solution extracted.

The effect of varying the solution acidity was examined with lanthanon and samarium. Solutions of 0·5 N lanthanon containing 0·25 N or 1 N acetic acid were extracted. More efficient extraction was obtained from the less acidic solution. The efficiencies were 30 per cent and 18 per cent for lanthanon, and 73 and 63 per cent for samarium respectively.

III. *The extraction of lanthanons with potassium and lithium amalgams*

These were carried out under identical conditions to those used for the sodium extraction, the alkali metal amalgams had similar molalities to the sodium amalgams.

It had been expected that these more electropositive amalgams would extract more of the lanthanon elements, but in fact only the same metals were extracted. These were, however, a number of differences in behaviour, which are summarized in Table 2. Overall efficiencies are given for the La-Nd group. The initial efficiencies were greater, but the same sequence followed. For the other three elements, the efficiency is the slope of the linear part of the extraction curve.

TABLE 2.—EXTRACTION OF LANTHANON SOLUTIONS (0·5 N) WITH 0·04 MOLAL AMALGAMS

Lanthanon	Extraction efficiency (%)		
	Li	Na	K
La	38	21	17
Ce	--	13	8
Pr	31	13	14
Nd	23	7	5
Sm	45	66	50
Eu	41	50	50
Yb	25	47	37

For the lower lanthanons, from lanthanum to neodymium, the most efficient extraction was obtained with lithium, and the sequence was Li > Na > K. Samarium, europium and ytterium, were again extracted more efficiently than the lower lanthanons but a different sequence Na > K > Li was found.

The reactivity of the three alkali metal amalgams to the hydrogen ion was compared by determining the alkali consumed when treated in an extraction column with a sodium acetate buffer (0 5 N, initial pH 4 20) With 0 04 molal amalgams, no difference in reactivity was observed

IV *Extraction of lanthanons in presence of alkali metal ions*

Since alkali metal ions from the amalgam accumulate in the aqueous phase during an extraction, it was of interest to examine the effect of adding the appropriate metal cation to the lanthanon solution The solutions examined were identical with those examined in section II and III, with the addition of appropriate quantities of alkali metal chlorides The following were examined La, Nd, Sm, Eu and Yb

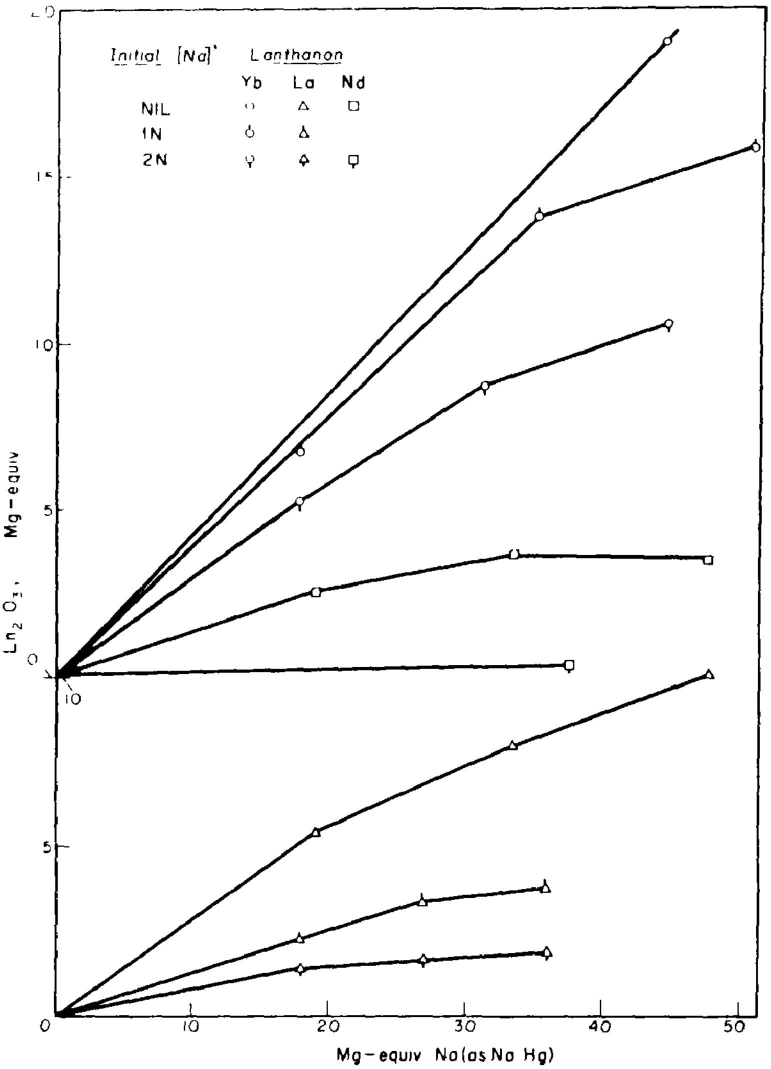


FIG 3 —Extraction of lanthanons in presence of sodium chloride

Addition of up to 2 N sodium chloride had no effect on the extraction of samarium and europium With ytterbium, little effect was found until the sodium concentration reached 2 N, but thereafter there was a substantial decrease in extraction efficiency Considerably larger effects were observed with lanthanum and neodymium With solutions of these two elements containing 2 N sodium chloride, 7 5 per cent of the lanthanum and 1 5 per cent of neodymium was extracted, compared with extraction of 20 and 7 per cent respectively in initially sodium-free solutions These results are summarized in Fig 3

V *The effect of solution and amalgam concentration on extraction*

In earlier work (Part I), it was observed that less samarium or ytterbium was extracted from dilute than from concentrated solutions This effect was investigated in more detail using La, Sm and Yb, the lanthanon acetate acetic acid ratio was 1 1

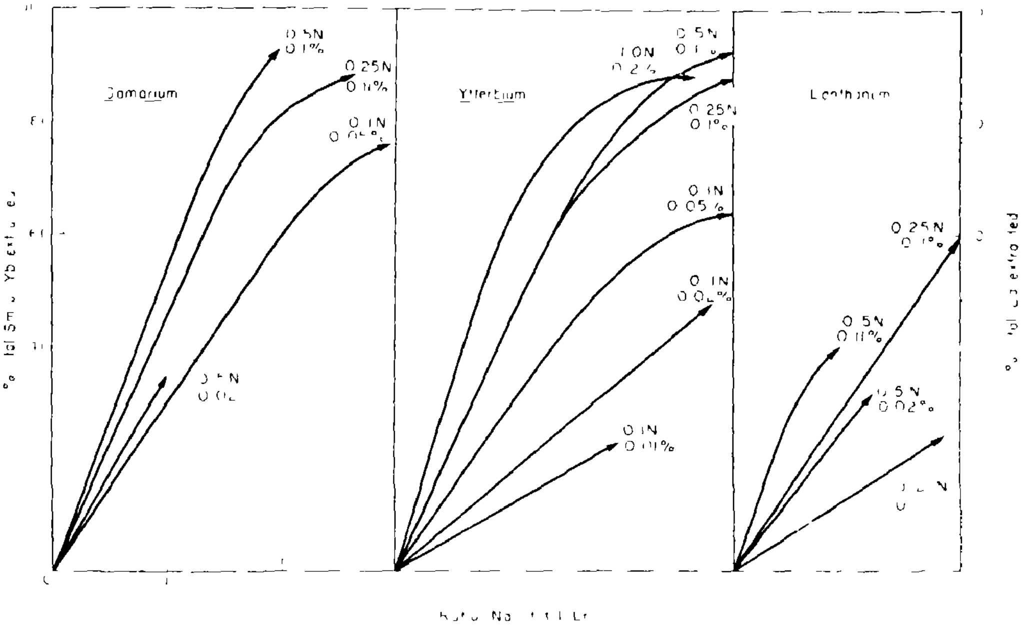


FIG 4 — Effect of solution and amalgam concentration on extractions

The simplest behaviour was observed with lanthanum Reducing the solution concentration to 0 25 N with a 0 1 per cent sodium amalgam, halved the extraction efficiency Similar large decreases in efficiency were found when a 0 5 N solution was extracted with more dilute amalgams (0 02% NaHg 9%) With samarium solutions, the extraction became less efficient on dilution (from 66 per cent in 0 5 N solution to 30 per cent in 0 1 N solution), and the total lanthanon extraction decreased from 95 to 80 per cent Very little effect was observed when the amalgam concentration was varied from 0 1 to 0 02 per cent, which confirmed the behaviour observed with complex samarium fractions

The extraction of ytterbium followed a similar pattern on dilution Unlike samarium, however, the extraction of ytterbium was affected by the amalgam concentration If this was lower than 0 05 per cent, extraction was less efficient, it was also increased, in the more concentrated solution, by use of more concentrated amalgams These results are summarized in Fig 4

In a number of these experiments, the change in sodium concentration in the amalgam phase was followed by flame photometry With samarium and ytterbium, less than 1 per cent of the sodium remained in the amalgam phase until the extraction efficiency decreased The amount of unreacted sodium then increased rapidly Different behaviour was found with lanthanum Even in the early stages of extraction, about 2-3 per cent of sodium was present in the amalgam phase and this increased steadily during the progress of extraction

VI *The extraction of binary mixtures of lanthanons*

The lanthanon elements form three groups in their behaviour towards alkali amalgams La, Ce, Pr and Nd extract with moderate efficiency, Sm, Eu and Yb with high efficiency, and the remainder do not extract Model systems were examined from these three groups

(a) *The effect of non-extractable lanthanons* Erbium was selected as a typical non-extractable lanthanon Binary mixtures were prepared with samarium or ytterbium total lanthanon and free acetic acid concentrations each being 0 5 N, and extracted with 0 1 per cent sodium amalgam The extraction curves are compared in Fig 5 with those obtained with samarium and ytterbium The extraction efficiency was less than could be accounted for by dilution of the extractable element, and material balance experiments showed that the sodium consumption was complete

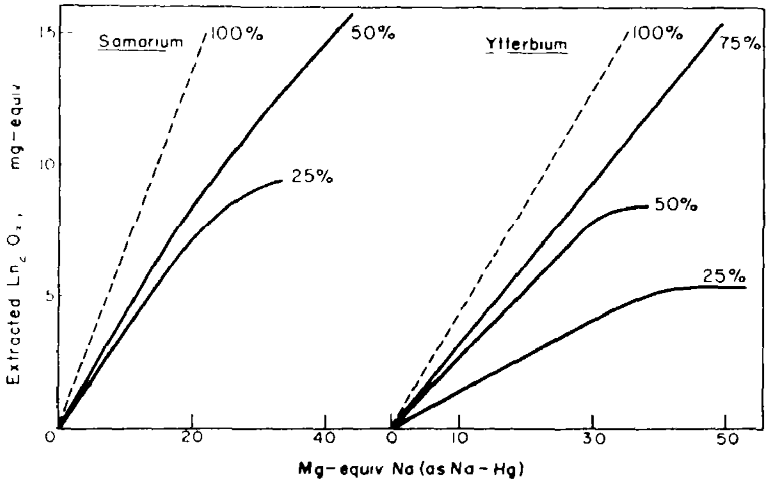


Fig 5 — Effect of erbium on extraction of samarium and ytterbium.

The reactivity of the three alkali amalgams to non-extractable lanthanons was compared 0 5 N solutions of yttrium and holmium acetate (pH 4 0) were treated in columns with 0 04 molal amalgams. Somewhat less metal reacted than in experiments with sodium acetate buffers, but a trend in reactivity was found in each case Lithium reacted more readily than the other two amalgams, the sequence being Li > K > Na.

(b) *Mixtures of extractable lanthanons* Binary mixtures of lanthanum with Sm or Yb were extracted similarly The behaviour of the solutions was intermediate between that of the components. Samarium or ytterbium were enriched in the amalgam phase (Table 3) If other elements from the La-Nd group were taken, the samarium content of the amalgam increased progressively The addition of 2 N sodium chloride effectively eliminated the extraction of neodymium

TABLE 3.—EXTRACTION OF BINARY MIXTURES OF LANTHANONS WITH SODIUM AMALGAM

La–Sm			La–Yb			Nd–Sm		
Sm in solution (%)	Amalgam, mg-eq Na	La in extract (%)	Yb in solution (%)	Amalgam, mg-eq Na	La in extract (%)	Sm in solution (%)	Amalgam, mg-eq Na	Nd in extract (%)
50	16.8	18	75	17.1	12	50	17.7	0.6
	32.7	19		38.6	12		31	0.9
	41.2	25		50.6	14		71	3.5
25	14.0	42	25	22.6	39	†	71	0.5
	24.2	42		45.1	33			
	30.3	37		64.4	31			

† In 2 N NaCl.

(c) *Mixtures of readily extracted lanthanons.* The elements Sm, Eu and Yb form a separate group. Solutions of pairs of these elements extracted at efficiencies of the order of 50 per cent, and their behaviour appeared to be additive. In all cases the composition of the extract was in good agreement with the original mixture, showing that these elements cannot be separated by amalgam extraction (Table 4).

TABLE 4.—EXTRACTION OF BINARY MIXTURES OF LANTHANONS WITH SODIUM AMALGAM

Sm–Eu			Sm–Yb			Eu–Yb		
Eu in solution (%)	Amalgam, mg-eq Na	Eu in extract (%)	Yb in solution (%)	Amalgam, mg-eq Na	Yb in extract (%)	Eu in solution (%)	Amalgam, mg-eq Na	Eu in extract (%)
50	15.8	47.4	25	27.1	28.5	46	15.8	40.1
	31.6	48.5	50	11.3	50.3		31.6	45.5
	67.8	49.5		18.1	49.6		54.3	40.5
				40.7	49.9			
			75	27.1	74.5			

VII. *The extraction of divalent europium*

The europous ion is the most stable divalent lanthanon ion in aqueous solution. The acetate was prepared by using a Jones reductor, aliquots were removed for determining the Eu^{2+} content of the solution iodometrically,(2) and the zinc content was determined on the polarograph.* Extraction was carried out with sodium amalgam and to obtain material balance the evolved hydrogen and change in zinc concentration were also determined. The results are shown in Table 5. Before extraction, all solutions contained $>95\%$ Eu^{2+} ion.

The maximum hydrogen evolution was less than 2 per cent of the sodium used for extraction. Disregarding the co-extraction of zinc, the europous ion was extracted with an efficiency of 80 per cent, Eu^{3+} extracted at 50 per cent efficiency. Similar large increases of efficiency were found when the divalent salt was extracted with lithium or potassium amalgam. The amount of zinc extracted in the three cases was in the electrochemical sequence Li K Na.

---

* When passed through a Jones reductor, slightly acidic europium solutions (pH 4) pick up somewhat more than the stoicheiometric quantity of zinc required by the reaction $2\,Eu^{3+} + Zn \rightarrow 2\,Eu^{2+} + Zn^{2+}$.

TABLE 5. EXTRACTION OF DIVALENT EUROPIUM WITH SODIUM AMALGAM

Amalgam mg-eq Na	Eu^{2+} extracted (mg-eq.)	Zn^{2+} extracted (mg-eq.)	Evolved H_2 (mg-eq.)	Eu + Zn + H_2 (mg-eq.)
13.05	10.85	1.75	0.1	12.7
26.1	20.83	5.03	0.4	26.25
30.0	23.87	4.7	0.6	29.17

When an equivalent quantity of zinc was added to a tervalent europium solution, no change was found in the extraction efficiency of the europium. The addition of erbium (0.25 N) to an Eu^{2+} solution caused no additional hydrogen evolution, and appeared not to affect the extraction. However, the additon of a similar quantity of lanthanum increased hydrogen evolution to 25 per cent of the sodium consumed, the two elements being co-extracted. The amalgam phase was enriched in europium.

ELECTROCHEMICAL MEASUREMENTS

I. *Polarography*

The redox potentials of Eu, Yb and Sm are well established by the work of McCoy, Laitinen and Glockler.(4, 5, 6) The main interest centred on further reduction steps of the lanthanon elements. Measurements were made on dilute (1 mmole/l.) lanthanon solutions, in an 0.1 M tetra-ethyl ammonium iodide supporting electrolyte. Gelatin was used as a maximum suppressor, and the pH of the solutions were adjusted in the range 3–4.

All further reduction steps were in the range from 1.6 to 1.8 V (hydrogen scale), and were very close to the breakdown voltage of the base electrolyte. It proved impossible to measure them with precision either by direct or derivative polarography.

II. *The potential of amalgam cells*

The e.m.f. of a number of alkali amalgam and lanthanon cells was measured, using the cell shown in Fig. 1. The types of cell examined were Na–Hg/NaOH/Hg–HgCl and Ln-Hg/Ln(OAc)$_3$/Hg–HgCl. Neutral lanthanon acetate solutions formed the electrolyte in the second type of cell. The e.m.f. of the amalgam cells was stable and could be reproduced satisfactorily, lanthanon amalgams, prepared by wet or dry methods agreed within 20 mV. A measurement was made on an Eu^{2+} solution. This was prepared with a Jones reductor, and the cell electrolyte also contained 0.5 N Zn(OAc)$_2$. The results are summarized in Table 6.

The e.m.f. values in column 5 are related to the standard potentials of the alkali metals and the rare earth metals. Values for the lanthanons are all lower than the alkali metal potentials, including the two "non-extractable" materials holmium and yttrium. The e.m.f. of the tervalent lanthanon cells are all lower than the reduction steps observed by polarography.

---

(4) H. N. McCoy, *J. Amer. Chem. Soc.* **58**, 1577 (1936).

(5) H. A. Laitinen, *J. Amer. Chem. Soc.* **64**, 1133 (1942).

(6) A. Timnick and G. Glockler, *J. Amer. Chem. Soc.* **70**, 1347 (1948).

TABLE 6.—E.M.F. OF AMALGAM CELLS

Amalgam	Amalgam concentration (w/w)	Amalgam molality	Electrolyte (1 N)	Cell e.m.f. (V)
LiHg	0.030	0.0432	LiOH	2.28
KHg	0.172	0.044	KOH	2.11
NaHg	0.100	0.0435	NaOH	2.09
LaHg	0.087	0.0053	$La(OAc)_3$	0.81
CeHg	0.110	0.0064	$Ce(OAc)_3$	1.04
PrHg	0.085	0.0049	$Pr(OAc)_3$	0.74
NdHg	0.087	0.0052	$Nd(OAc)_3$	0.69
SmHg	0.095	0.0055	$Sm(OAc)_3$	1.80
EuHg	0.098	0.0056	$Eu(OAc)_3$	0.75
EuHg	0.101	0.0058	$Eu(OAc)_2$	1.10
YbHg	0.120	0.0061	$Yb(OAc)_3$	1.52
HoHg	0.093	0.0050	$Ho(OAc)_3$	1.07
YHg	0.085	0.0075	$Y(OAc)_3$	1.28

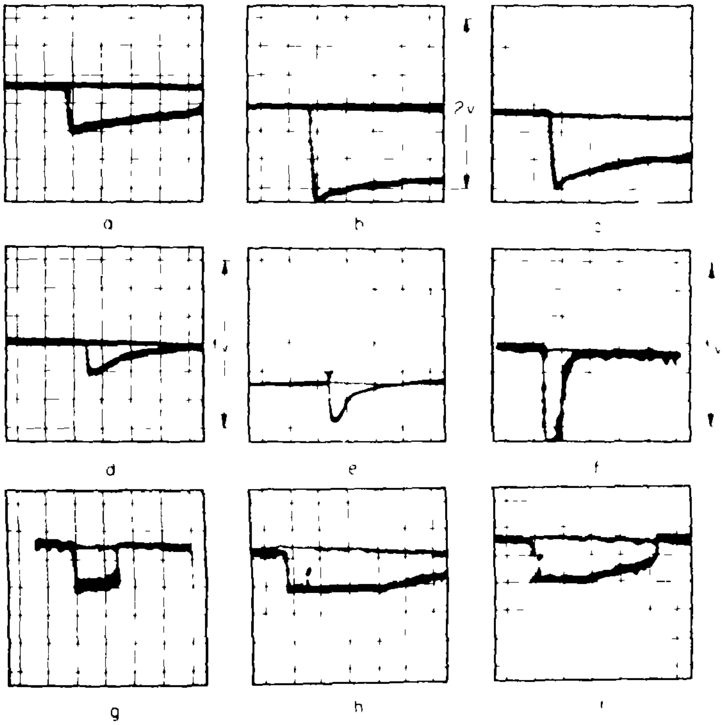


FIG. 6.—Potential changes of sodium amalgam drops in lanthanon solutions

Vertical scale: 0.5 V per scale division, except where marked. Horizontal scale: 1 sec per scale division

(*a*) La	(*b*) Pr	(*c*) Nd
(*d*) Sm	(*e*) Eu	(*f*) Yb
(*g*) Eu^{2+} + 0.5 N Zn	(*h*) Zn	(*i*) Eu^{2+} + 1 N Zn

III *Potential changes of amalgams during extraction*

The cell just described was used, with a sodium amalgam cathode The changes of e m f with time were followed with an oscilloscope In this case, the pH of the lanthanon electrolyte (1 N) was adjusted to 5 0 to prevent excessive hydrogen evolution, which produced much "noise" on the oscilloscope trace

The behaviour of the groups of lanthanon elements are illustrated in Fig 6 A freshly formed sodium amalgam drop momentarily gave the characteristic sodium potential With La, Pr and Nd, the e m f decreased slowly with time, a steady value being approached in 15″-20″ (a, b, c) The e m f changes were more rapid with Sm, Eu and Yb, (d, e, f), and were usually complete within 2″ These times were prolonged by dilution of the electrolyte The final e m f of the amalgam drop, corresponding to the horizontal trace on the oscillograms, was in reasonably good agreement with the amalgam cell e m f's of Table 6

A different type of behaviour was observed with divalent europium Two waves were found with a (1 N Eu^{2+} + 0 5 N Zn^{2+}) electrolyte (*g*) The first wave appeared to be characteristic of the reduction of zinc (*h*) as addition of more zinc to the original electrolyte extended the first wave (*i*) A zinc amalgam electrode had a lower e m f (1 01 V) than the Eu^{2+} amalgam electrode potential In this case, it appeared that the first step was a slow reduction of zinc, followed by a rapid reduction of Eu^{2+}

In solutions of non-extractable lanthanons the e m f of the sodium electrode remained unchanged over a period of ten minutes.

DISCUSSION

This work shows that the amalgam extraction of the rare earth elements is considerably more complex than deduced from the earlier work on lanthanon fractions containing varying quantities of samarium or ytterbium Marginal quantities of the light lanthanon elements were extracted under these conditions, and it was suggested that this was due to small differences in potential of the Na/Hg and Ln/Hg electrodes It was also suggested that the potential of the non-extractable lanthanons was greater than the sodium electrode The experiments described here do not substantiate this hypothesis

Experiments on the stoicheiometry of the extraction process show that the simple overall reaction suggested by Equations (1)–(3) is followed, but as already stated, certain reservations must be made Also, considering the extraction data obtained over a wide range of conditions, the decrease in extraction efficiency observed when the lanthanon concentration has been depleted is consistent with a change in kinetic mechanism in the dilute solutions The extraction process is clearly electrochemical, but a more detailed examination shows a number of inconsistencies A polarographic examination of the rare earth elements gave reduction waves at 1 6–1 8 V, which could not be resolved Reduction steps at appreciably lower voltages would be predicted from the e m f of the lanthanon amalgam cells Only seven of the lanthanon elements are extracted, which would not be predicted on electrochemical grounds The La–Nd group of elements extract with the alkali metals in the sequence Li > Na > K, which is not the electrochemical sequence. The amount of extraction decreases in order of atomic number, the opposite effect would be predicted from the electrochemical data of Table 7, although there is a small trend in the expected direction with cerium The Sm-Eu–Yb group extract with considerably greater efficiency, divalent ions are formed during extraction, and all extract in the abnormal sequence Na > K > Li The amount of extraction again decreases with atomic number, and is unrelated to the stability of the divalent ions in solutions since the element having the least stable divalent ion (Sm) is extracted with the highest efficiency Also, while the three alkali amalgams showed equal reactivity to the hydrogen ion, they were less reactive in solutions of the non-extractable lanthanons, and the alkali consumption was in the electrochemical sequence Li > K > Na These facts suggest that the net effect observed in an extraction experiment is the sum of two divergent mechanisms The techniques used in this work were not suited for the study of kinetic mechanisms, nevertheless the experimental results are consistent with a fairly simple pattern

The acetate ligand forms a series of complex ions with rare earth cations, but the amount of complexing is small (β_1 40–1000) and shows no major trend with atomic number (7) The reduction process will therefore be discussed in terms of lanthanon cations Conductivity measurements show that the size of the hydrated rare earth cations increases with atomic number (8) This increase in hydration explains the increased tendency of rare earth cations to hydrolyse from lanthanum to lutecium (9 11) The surface of an alkali amalgam drop is alkaline, and early experiments with neutral lanthanon solutions were abandoned because of hydroxide precipitation To prevent this, and control the reaction of the amalgam with hydrogen ions, a buffered system was adopted (1) BIEDERMANN has shown that lanthanum solutions, at pH's above 6 5 contain hydrolysed and polynuclear species such as $La(OH)^{2+}$ and $La_2(OH)^{5+}$ (12) It is logical to expect the formation of hydrolysed species at lower pH's with an increase in atomic number

A hydrolysis mechanism, involving the formation of non-reducible polynuclear species, explains many of the experimental facts, in particular the general tendency for extraction to decrease with atomic number and the behaviour of the non-extractable lanthanons

$$Ln^{3+}\ nH_2O + Na \rightarrow Ln(OH)^{2+} + Na^+ + H$$

When the hydrolysed lanthanon is mixed with the bulk solution, hydrolysis is reversed, so that the mechanism is equivalent to a catalysed evolution of hydrogen

$$Ln(OH)^{2+} + H^+ \rightarrow Ln^{3+} + H_2O$$

There is no evidence for the formation of intermediate ions in the extraction of the La–Nd group of elements In fact, "divalent" salts of these elements appear to have semi-metallic properties (13 14) Quantitatively, extraction is very inefficient, for example the probability of a sodium atom reacting with H^+ is 10^4 greater than reduction of La^{3+} The extraction is slow, as shown by the extraction experiments and confirmed by the electrokinetic evidence It is concluded that reduction takes place by a three-electron step, the extraction being the sum of opposed electrochemical and hydrolytic effects Experiments with non-extractable lanthanons showed them to hydrolyse in the sequence Li > K > Na, so the concentration of unhydrolysed material would vary in the reverse sequence This is a reasonable explanation of the observed extraction sequence, Li > Na > K The anomaly between the polarography of the rare earth elements, and the EMF of the amalgam electrodes, can be resolved if the reduction is a slow process [(15)]

---

(7) A SONESSON, *Acta Chem Scand* **12,** 165, 1937 (1958)

(8) F H SPEDDING and G ATKINSON, *The structure of Electrolytes* (Edited by W J HAMER) p 319 J Wiley, New York (1959)

(9) H T S BRITTON, *J Chem Soc* **127,** 2142 (1925)

(10) T MOELLER and H F KREMERS, *J Phys Chem* **48,** 395 (1944)

(11) T MOELLER and N FOGEL, *J Amer Chem Soc* **73,** 4481 (1951)

(12) G BIEDERMANN and L CIAVATTA, *Acta Chem Scand* **15,** 1347 (1961)

(13) J D CORBETT, L F DRUDING and C B LINDAHL *J Inorg Nucl Chem* **17,** 176 1961

(14) L F DRUDING and J D CORBETT, *J Amer Chem Soc* **81,** 5512 (1959), **83,** 2462 (1961)

Since hydrolysis increases with atomic number, a continuation of the trend observed with the La–Nd elements makes a three-electron reduction unlikely for the Sm–Eu–Yb elements Divalent ions are formed during the extraction of this group of elements, and it is probable that reduction to the metal proceeds exclusively by this route The extraction of the Eu^{2+} ion by amalgams is very efficient, since it was extracted with a negligible evolution of hydrogen There is a well-known similarity between the divalent rare earth ions and the alkaline earths, hydrolysis is probably slight, since europous hydroxide is appreciably soluble in alkaline solution If it is assumed that the tervalent cations are subject to hydrolysis in the sequence Li > K > Na, unhydrolysed cations will be available for stepwise reduction in the opposite sequence, namely Na > K > Li, which is found experimentally

There are three further points that call for comment The addition of sodium chloride to solutions of the La–Nd group of lanthanons considerably decreased the extraction In the Sm–Eu–Yb group, no effect was observed with the first two elements but at high sodium chloride concentrations the extraction of ytterbium was decreased There is no evidence of chloride complexing of the lanthanon elements [(16)] The effect is probably statistical, being equivalent to dilution of the lanthanon solution Under these conditions, hydrolysis or the reaction of sodium with hydrogen ions is more probable than a three or two-electron reduction

No separation of mixtures of the Sm–Eu–Yb group of elements was obtained by extraction This would require an equal amount of hydrolysis of each species at the amalgam interface, and the two-electron reduction potential of the reduced species to be identical Such a coincidence appears improbable There is, however, evidence from electron transfer reactions of charge transfer mechanisms involving solvent molecules It seems likely that a mechanism of this type is necessary to explain the experimental findings

The e m f's of the lanthanon amalgam cells given in Table 7 are related to the standard potentials of the elements The standard potential is the sum of the amalgam potential and terms related to the solution and metal activities LATIMERS' values for the standard potentials of the lanthanon elements decrease in a regular sequence from La = −2 52 V to Ln −2 25 Volts [(17)] There are marked divergences in the experimental data, and it would appear that LATIMERS' values are open to question

Acknowledgements—We would like to thank DR M E PFOVER for a discussion and MR G SMITH for a number of sodium estimations This work forms part of the programme of the National Chemical Laboratory and is published by permission of the Director

---

[(15)] M E PLOVER, *J Chem Soc* 4540 (1962)

[(16)] K A KRAUS and F NELSON, *Proceeding of the International Conference on the Peaceful Uses of Atomic Energy, Geneva,* 1955, Vol 7, p 113 United Nations (1951)

[(17)] W M LATIMER, *Oxidation Potentials* Table 69, p 291 Prentice-Hall, New Jersey (1959)

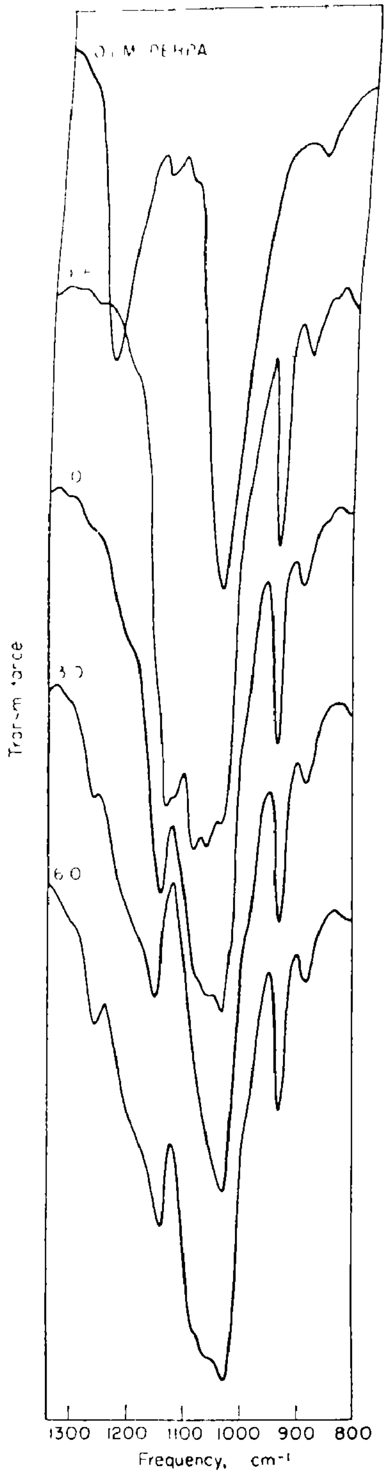


FIG. 5. Infra-red spectra organic phases from the extraction of uranyl nitrate solutions (25 g/l.) containing nitric acid with 0.1 M DEHPA in kerosene (figures on curves are nitric acid concentrations, M)

J. Inorg. Nucl. Chem. 1963. Vol. 25, pp. 1287 to 1291. Pergamon Press Ltd. Printed in Northern Ireland

SOLUTION OF METALS IN THEIR MOLTEN SALTS
SOME MANGANESE, CHROMIUM, URANIUM AND ANTIMONY SYSTEMS*

J. D. Corbett, R. J. Clark and T. F. Munday
Institute for Atomic Research and Department of Chemistry
Iowa State University, Ames, Iowa

(*Received* 17 *January* 1963)

Abstract—Preparations of high purity $MnCl_2$, $CrCl_2$, CrI_2, UBr_3, UI_3 and Sb_2S_3 are described, the melting points obtained for CrI_2 (868) and Sb_2S_3 (559.5) are significantly higher than previously reported. The small solubilities of manganese and chromium in the respective halides studied were characterized primarily by the depression of the freezing points of the salts by excess metal. For $MnCl_2$ + Mn (in Ta), ΔT is 1.5 ± 1, for $CrCl_2$ + Cr, 6, and for CrI_2 + Cr, 3.

The UBr_3–U and UI_3–U systems were studied by equilibration in tantalum containers followed by analysis of the saturated salt phase. Uranium dissolves in liquid UBr_3 to 4 ± 1 mole per cent over the range of 800–912, and in UI_3(l), from 5.7 per cent at 784 to ~9 per cent at 1020. The liquidus curve for Sb_2S_3 + Sb was investigated by thermal analysis, the salt-rich eutectic is at 524.5 and 18.0 ± 0.5 per cent Sb. At 780 the equilibrium salt phase contains 42.0 ± 0.5 per cent Sb. The UBr_3 and Sb_2S_3 compositions are somewhat lower in metal content than previously reported.

HITHERTO the only knowledge of metal–metal halide interactions for metals of the first transition series has been for nickel, where solutions of up to 9 mole per cent metal in liquid $NiCl_2$ have been observed.[1] Investigation of the system $MnCl_2$–Mn was prompted principally by the report[2] that use of the thermodynamic half cell potential for a $Mn/MnCl_2$ reference cell gave a potential for the U/UCl_3 couple 0.1 V lower than obtained with $Fe/FeCl_2$ or Ag/AgCl. This suggested that an appreciable solution of Mn in liquid $MnCl_2$ may have been responsible for the observed deviation even though one possible solution mode, the formal reduction of the $3d^5$ solvent ion Mn^{2+}, could be considered unusual. Conversely, the CrX_2–Cr systems X = Cl, I have been examined to establish whether the simple Cr^+ ion might possess a stability sufficient to exist in a more or less dilute solution in liquid CrX_2.

An appreciable solution of uranium metal in certain of the liquid uranium (III) halides has been reported. With UCl_3, this has been given as 4 per cent metal at 820°, the eutectic, and 6 per cent at 1140°,[3] while in UBr_3 a much larger dependence of solubility on temperature has been suggested, increasing from about 4 per cent at the eutectic (743°) to roughly 21 per cent at only 950°.[4] In view of the admittedly tentative nature of the published results for the bromide system and also the probable presence of side reactions with the containers used in the prior study, the system has been re-examined. In addition, reaction of $UI_3(l)$ with metal has been explored to establish whether the trend suggested by the above chloride and bromide data would result in an even larger interaction in this case, or perhaps the separation of a lower phase.

---

* Contribution No. 1268. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

[1] J. W. Johnson, D. Cubicciotti and C. M. Kelley, *J. Phys. Chem.* **62**, 1007 (1958).

[2] E. D. Eastman, J. A. Campbell, D. Cubicciotti and M. J. Sienko, *The Chemistry of Uranium, Collected Papers* (Edited by J. J. Katz and E. Rabinowitch), TID-5290, Book 1. Paper 21 USAEC, Oak Ridge, Tenn. (1958).

[3] D. Cubicciotti, MDDC-1058, p. 12. Technical Inform. Branch, Oak Ridge Nat'l Lab. Oak Ridge, Tenn. (1947).

[4] E. D. Eastman, C. D. Thurmond and R. A. Webster, *The Chemistry of Uranium Collected Papers* (Edited by J. J. Katz and E. Rabinowitch) Paper 24. TID-5290, Book 1, USAEC Oak Ridge (1958).

Finally, the Sb_2S_3 system presents an interesting example of a relatively large solubility of metal, 20 to 30 per cent at the eutectic at 520°(5,6) and 42 per cent at 615°, the monotectic,(7) without the formation of an intermediate phase. As is frequently the case with chalcogenide vs. halide systems, the interaction is far greater than in the corresponding halides, where formation of Sb_2I_4 is indicated in the iodide melt.(8) In similar contrast, the sulphide melts apparently show a definite electronic conductivity with relatively large amounts of dissolved metal.(7) Inasmuch as a technical grade of Sb_2S_3 was employed in recent studies of the system, the Sb_2S_3 liquidus curve as well as the solubility of liquid metal at 780° have been reinvestigated with higher purity materials.

EXPERIMENTAL

$MnCl_2$–Mn. The salt was prepared by dehydration of the reagent grade tetrahydrate under anhydrous HCl at 500°, followed by treatment with Cl_2 up to 700°, and vacuum distillation at 800°. The chlorination step was found necessary in order to obtain a clear, yellow-brown melt without deposition of a black solid. The metal (99.9 per cent A. D. MacKay) attacked Vycor in the presence of molten $MnCl_2$ so that thermal analysis studies were carried out in tantalum containers, and then only with excess metal because of the simultaneous formation of a $TaMn_2$ coating on the container. Thermocouples were periodically checked against the melting point of NaI. Separate $MnCl_2$ samples gave melting points of 653.5 and 654°, each ± 1°, compared to 650° given by MOORE.(9)

$CrCl_2$–Cr. Since preparation of $CrCl_2$ via H_2 or HCl treatment of $CrCl_3$ or Cr respectively could give a product contaminated with one or the other starting material which would thereby vitiate subsequent results, the stoicheiometric compound was prepared from $CrCl_3$ and Cr. Reaction of the metal (Electromet 99.9+ per cent) with dry Cl_2 at 960° gave $CrCl_3$, and this was sublimed under Cl_2. The proper proportions of metal and $CrCl_3$ (to ± 0.001 in Cl/Cr) were then reacted completely (without exposure to the atmosphere) in a sealed, fused silica container at 890° to give the pure, asbestos-like $CrCl_2$. Thermal analyses were performed in sealed glass containers, with weighed amounts of metal added through a break-seal. The melting point of $CrCl_2$ was found to be 824°, compared to the "selected" 815°(10) and 824° reported by FISCHER and GEWEHR.(11)

CrI_2–Cr. Metal at 800° was reacted with I_2 from a reservoir at 175° in a sealed, evacuated, glass container to give a mixture of CrI_2 and CrI_3. Sublimation of this product *in vacuo* at 700° gave the red-brown CrI_2 plus a trace of the black CrI_3, with metal in the residue and considerable amounts of I_2 in the cold trap. Additional vacuum sublimation continued to give small amounts of CrI_3 in the product. This was finally removed by sublimation from the CrI_2 in a sealed tube at 555°. Alternatively, Cr and I_2 in stoicheiometric proportions (± 0.001 in I/Cr) were transferred in an inert atmosphere box and reacted to produce CrI_2, red in transmitted, and yellow-brown in reflected light. Both products gave a melting point of 868° in sealed tubes, which is far in excess of the 790–795° inferred by HEIN and WINTNER-HOLDER from resistance measurements.(12)

---

(5) F. M. JAEGER and H. S. VAN KLOOSTER, *Z. Anorg. Chem.* **78**, 245 (1912).

(6) H. PELABON, *Ann. Chim. Phys.* **17**, 530 (1909).

(7) T. YANAGASE and G. DERGE, *J. Electrochem. Soc.* **103**, 303 (1956).

(8) B. L. BRUNER and J. D. CORBETT, *J. Inorg. Nucl. Chem.* **20**, 62 (1961).

(9) G. MOORE, *J. Amer. Chem. Soc.* **65**, 1700 (1943).

(10) *Selected Values of Chemical Thermodynamic Properties*, Series II, Table 49-1. Nat'l Bur. Stds., Circular 500, U.S. Gov't Printing Office, Washington, D.C. (1950).

(11) W. FISCHER and R. GEWEHR, *Z. Anorg. Chem.* **222**, 308 (1935).

(12) FR. HEIN and I. WINTNER-HOLDER, *Z. Anorg. Chem.* **202**, 81 (1931).

UBr_3-U UBr_4 was used as the starting salt since it could be readily sublimed to reduce impurities The metal was cut from a rod (Mallinckrodt, principal metallic impurities, in ppm 50 Fe, 44 Al, 14 Mg) and cleaned with 1 1 HNO_3 while the bromine (0 02 per cent Cl, A D MacKay) was dried over P_4O_{10} and subsequently sealed in ampoules equipped with break-seals The Br_2 container and the metal were placed in opposite ends of a Vycor tube in the form of a shallow, inverted V, and this was evacuated Hydrogen, purified by passage through a trap filled with Linde Molecular Sieve 4A cooled to −196°, was reacted with the metal at 250 for 1–2 hr, and the hydride so formed then decomposed under vacuum at 500° The apparatus was then sealed, the spectacular reaction initiated by breaking the ampoule, and completed by heating the metal end to 570° and the Br_2, to 40 to 50

Purification of the UBr_4 by sublimation at 450° plus all subsequent UBr_4 U reactions were executed in Ta so as to eliminate side reactions with glass For the first step a two-piece, Ta apparatus was constructed from ¾ in tubing so as to provide an extended crucible for the crude material and a closely fitting cylinder on the open end for the condensate The UBr_4 product had an average Br content of 57 43 per cent vs the theoretical 57 32 per cent

Known quantities of U and UBr_4 were contained in ¼ in 2 in Ta tubes arc welded under ~⅓ atm of He These were heated in a glass container under proportional temperature control with measuring thermocouple junction in contact with the metal wall, and were quenched by dropping them into a silicone oil reservoir in the bottom of the glass envelope The composition of the salt phase was usually determined from the loss in weight of the added metal, as the massive U did not disintegrate at or below 915 , the adhering salt could be easily removed by a H_2O wash, and an appreciable solubility of salt in the solid metal was not evident Direct analysis of the salt phase was in good agreement when checked, for example, 49 30 per cent Br vs 49 36 per cent calculated from the weight loss The product gave a powder pattern of only UBr_3 Analysis for bromide was gravimetric, the silver precipitated by reaction of the ion with U(IV) was redissolved by heating for an hour with dil HNO_3

UI_3-U Preparation and purification of the pure uranium iodides is more difficult due to the ease of disproportionation or dissociation To avoid reaction of UI_3 with glass at elevated temperatures the synthesis procedure used for the rare earth metal triiodides[13] was employed, so that metal in a W crucible at 800 reacted with I_2 vapour from a reservoir at 100–120 The reaction was still slow and incomplete, and massive metal remained after 48 hr Reaction of iodine with powdered "hydride" U was more successful, giving a product $UI_{2\ 95}$ (99 87 per cent I + U) with a melting point of 771–772° (766 5 ± 1° lit [14]) Thermal analysis and equilibration experiments were again carried out in sealed Ta tubes, in this case recrystallized metal was evident in the salt matrix after 3 hr at 1020 so that salt analysis rather than weight loss of the metal was more reliable at the higher temperatures Because ready sublimation of the iodide was not feasible some oxygen contamination is to be expected, 0 1 per cent was found in one sample by inert gas fusion Reduced salts showed only the powder pattern of UI_3

Sb_2S_3–Sb Technical Sb_2S_3 (Fisher) was found to have very unsatisfactory melting characteristics, and spectrographic examination showed major amounts of Si Fe Ca and Cu Although vacuum sublimation gave a considerably better material, the majority of the starting salt used was synthesized from the elements Purified sulphur was vacuum sublimed at 140°, discarding about the first and last third, and was subsequently handled only in a dry-box The metal, 99 999 per cent with respect to metal content (A D MacKay), was fused in vacuum to reduce the oxide content The elements were reacted in the desired proportions in evacuated and sealed glass tube as before, with the metal heated to about 600 and the sulphur, to 400 For pure Sb_2S_3 rather than mixtures, a final vacuum sublimation at 540° was added Spectrographic analysis of this showed only traces of Pb and Si, and the melting point of 559 5° obtained compares to 547 in a recent compilation[15] and 546 in the most complete phase diagram of the Sb_2S_3-Sb system [ ]

The Sb_2S_3 liquidus curve was studied on mixtures synthesized *in situ* from the elements equilibrated at 600–650° in the sealed Vycor cell, and cooled at 1–5 min^{-1} The thermocouple calibrated by the 630 5° melting point of the metal was contained in a well projecting into the melt Serious supercooling was reduced by the presence of powdered Vycor and by mechanically shaking the entire cell through an attached quartz rod operated by a motorized cam. Compositions were altered by sublimation of the entire contents of the cell through a break-seal into a like cell containing additional metal.

---

[13] L F DRUDING and J D CORBETT, *J Amer Chem Soc* **83**, 2462 (1961)

[14] M M POPOV and M D SENIN, *Zh Neorg Khim* **2**, 1479 (1957)

[15] *Selected Values of Chemical Thermodynamic Properties*, Series II Table 21–22 Nat'l Bur Stds Circular 500, U S Gov't Printing Office, Washington, D C (1950)

Since the above data disagreed noticeably with previous results, the composition of the salt-rich phase in equilibrium with liquid Sb at 780° was also checked. Known weights of Sb and sublimed Sb_2S_3 were equilibrated in short lengths of sealed Vycor tubing, cooled quickly, and the recovered metal button was cleaned with aqu. HCl and weighed. In order to correct for the significant solubility of salt in liquid metal that was retained within the button, values of the apparent solubility vs. wt ratio of metal to salt at equilibrium for several experiments were extrapolated back to zero metal phase. The result agreed to within 0.1 per cent dissolved metal with that obtained directly through use of a button previously saturated with salt. Powder pattern data confirmed that a new solid phase is not formed.

RESULTS AND DISCUSSION

Metal interactions with the liquid manganese and chromium halides were found to be so small that direct methods for the determination of the composition were concluded to be generally unreliable. Accordingly, the magnitude of the solubility was inferred from the depression of the freezing point of MX_2 by added metal. Excess Mn lowers the $MnCl_2$ point by only 1.5 ± 1°, from the calorimetric heat of fusion(9) this corresponds to an ideal solution of about 0.8 ± 0.5 mole per cent Mn as atoms, or half as much as Mn^+. With $CrCl_2$ + Cr, the liquidus data for mixtures containing 0.7–6 per cent Cr indicate a eutectic at 818 ± 1°, a depression of 6°, with the composition near 3–4 per cent. A composition of 1.9 per cent metal as atoms is calculated from the ΔT of 6° and the accepted(10) heat of fusion. The 868° melting point of CrI_2 is depressed only 3° by excess chromium, so any reaction must be even less favorable than with the chloride.

Metal interactions of this sort as possible evidence for monovalent ions of the first transition series thus continue to be substantially negative other than for nickel and, of course, its neighbour copper. Indirect evidence suggests a similarly negligible reaction in $FeCl_2$–Fe,(2) while metal solution in molten CoI_2 appears very minor.(16)* The behaviour of this series may be roughly correlated with fundamental thermodynamic quantities to the extent that the relative enthalpy for the solution reaction $M^{2+} + M \rightarrow 2M^+$ will be more favourable for a small value of $(I_1 - I_2 + \Delta H_{subl})$ for the element M. These terms for the elements Ti to Cu clearly support the predominance of Cu^+ and indicate that Ni^+ and Cr^+ should be next most stable, with Mn^+ in fourth place. The difference observed experimentally in the amount of reaction of Cr and Ni with their chlorides amounts to a free energy difference of only about 2 kcal per mole of the M^+ presumed formed, and this scarcely could have been predicted by such means.

The solution of U in UBr_3 was investigated between 800 and 915°. The solubility of 4 ± 1 per cent is substantially independent of temperature within the reproducibility of the measurements although there may be a small retrograde solubility effect within the quoted uncertainty. This amount agrees with the approximate 3 to 5 per cent at the 743° eutectic concluded earlier(4) (although their experimental data appear to allow this composition to be as high as 8 per cent). On the other hand, the much greater metal content in the liquidus compositions previously reported at higher temperatures must have been due to extensive attack of the alumina and porcelain apparatus

---

* The solubility, ~2 ± 1 per cent, was estimated directly by analysis of the saturated salt phase and is probably a maximum value.

(16) S. V. WINBUSH Thesis, Iowa State College (1956).

Investigation of the UI_3–U reaction was not carried out extensively when it became apparent that the solubility was not significantly greater than in the bromide At 784°, about 18° above the reported(11) melting point, the solubility is 5 7 per cent and this increases to 6 3 per cent at 865° and ~9 per cent at 1020° Uranium (II) would thus appear to have only a very limited stability Incidentally, it was also established that UI_3 exhibits a very high resistance typical of a salt This eliminates the possibility, apparently not previously clarified, that UI_3 might be a metallic salt (e g $U^{4+}(I^-)_3e^-$) such as recently found with ThI_2 (17)

The improved quality of the Sb_2S_3 indicated by the higher melting point obtained also resulted in a significant change in the liquidus curve obtained on addition of metal The temperatures observed (+1°) for the respective mole per cent of dissolved metal (±0 1 per cent) (based on Sb_2S_3 solvent) are 551 5°, 4 3, 547, 7 8, 533, 14 0, 526, 16 5, 529, 16 7, 524, 17 8, with the eutectic temperature at 524–5° The eutectic composition of 18 0 ± 0 5 per cent when compared to the earlier 21 per cent at 520°(5) and about 30 per cent at 519 (6) suggests that oxidizing impurities may have been present in the salt used previously Similarly, the sulphide-rich phase in equilibrium with the liquid metal-rich phase at 780° was found to contain 42 0 ± 0 5 per cent metal, somewhat less than the 48 per cent interpolated from the most recent data (7)

Analysis of the above liquidus data in terms of Sb + Sb_2S_3 mixtures gives a limiting heat of fusion of 8 9 kcal per mole of Sb_2S_3, compared to 5 6 kcal mole^{-1} in the literature (5) The latter, or actually twice this value, was deduced from the liquidus curves for solutions of SnS and PbS in what was presumed to be the molecular solvent Sb_4S_6 In the absence of more specific knowledge of the solvent characteristics and constitution of liquid Sb_2S_3, the only substantial conclusion that can be reached is that Sb metal effectively produces about one-third fewer solute particles on solution in Sb_2S_3 than do SnS or PbS

---

(17) R J Clark and J D Corbett, *Inorg Chem* **2**, 460 (1963)

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 1293 to 1300. Pergamon Press Ltd. Printed in Northern Ireland

NOTES

Thermal decomposition of plutonium oxalates

(*Received* 18 *February* 1963, *in revised form* 23 *April* 1963)

THE THERMAL decomposition of plutonium oxalates has been studied to clarify some of the discrepancies reported in the literature. DAWSON and ELLIOTT[1] have indicated the formation of an intermediate of indefinite composition at about 200°C during the thermal decomposition of plutonium(IV) oxalate. KARTUSHORA *et al.*[2] have shown that partial reduction takes place in the thermal decomposition of plutonium(IV) oxalate, and that the thermal decomposition of plutonium(III) oxalate in an inert medium at 330°C produces an oxalate-carbonate for which they have assigned the structure $Pu(C_2O_4)(CO_3)_{0.5}$. MYERS[3] reports that an intermediate product, probably plutonium oxyoxalate $Pu_2O_2C_2O_4$ is formed during the decomposition of plutonium(IV) oxalate in an inert atmosphere at 260–275°C but the product has not been conclusively identified.

Our study of the thermogravimetric decomposition of plutonium(IV) oxalate hexahydrate in air has shown a definite intermediate of trivalent plutonium in the temperature range of 250–280°C, which has been characterized by chemical analysis as an oxalate-carbonate, viz. $Pu(C_2O_4)(CO_3)_{0.5}$ (requires Pu 66.9, $C_2O_4^{2-}$ 24.7, CO_3^{2-} 8.4%, found Pu 65.4, $C_2O_4^{2-}$ 25.3, CO_3^{2-} 8.6%). The full thermal decomposition curve is shown in the graph.

Plutonium(III) oxalate precipitated from aqueous solution was found to crystallize with ten molecules of water and not nine molecules as has been noted previously.[4] This has been confirmed by X-ray analysis which showed the compound to be iso-structural with lanthanum oxalate decahydrate. On heating on the thermobalance in air, hydrates containing 9, 2 and 1 molecule of water of crystallization were obtained, while in an argon atmosphere the anhydrous oxalate was also formed. There was no indication of intermediate compounds between the anhydrous oxalate and the final product plutonium dioxide.

Experimental

Preparation of plutonium oxalates. Plutonium (IV) oxalate hexahydrate was prepared by adding 0.6 M oxalic acid to an ion exchange purified solution of plutonium (IV) in 2N nitric acid. Plutonium (III) oxalate was precipitated by adding 0.6 M oxalic acid to a solution of plutonium which had been reduced to this valency state by hydroxylamine hydrochloride. The tri- and tetravalent oxalates were stored dry for a maximum of 2 weeks and the trioxalate was stored in an argon atmosphere.

TABLE 1. THERMAL DECOMPOSITION OF PLUTONIUM(IV) OXALATE

Probable formula	Observed molecular weights in runs						Temperature range of stability
	1	2	3	4	5	6	
$Pu(C_2O_4)$ (415) or $Pu(C_2O_4)\cdot H_2O$ (433)	425	416	429	411	420	428	100°–175°C
$Pu(C_2O_4)(CO_3)_{0.5}$ (357)	360	362	358	361	344	365	250°–280°C

---

[1] J. K. DAWSON and R. M. ELLIOTT, AERE-C/R 1207.

[2] R. E. KARTUSHORA, T. I. RUDENKO, and V. V. FOMIN, *Atomnaya Energiya* 5, No. 1 pp. 24–29 (1958).

[3] M. N. MYERS, HW-45128.

[4] G. T. SEABORG and J. J. KATZ, *The Actinide Elements* p. 420, McGraw-Hill, New York.

TABLE 2 THERMAL DECOMPOSITION OF PLUTONIUM(III) OXALATE

Atmosphere	Probable formula	Observed molecular weights in runs 1	2	Temperature range of stability (°C)
Air	$Pu_2(C_2O_4)_3 \cdot 10H_2O$ (922)	920	930	Up to 40
	$Pu_2(C_2O_4)_3 \cdot 9H_2O$ (904)	905	915	55–70
	$Pu_2(C_2O_4)_3 \cdot 2H_2O$ (778)	780	778	125–150
	$Pu_2(C_2O_4)_3 \cdot H_2O$ (760)	763	760	175–195
Argon	$Pu_2(C_2O_4)_3 \cdot 10H_2O$ (922)	923	916	Up to 25
	$Pu_2(C_2O_4)_3 \cdot 9H_2O$ (904)	891	901	40–60
	$Pu_2(C_2O_4)_3 \cdot 2H_2O$ (778)	780	779	150–175
	$Pu_2(C_2O_4)_3 \cdot H_2O$ (760)	762	762	215–235
	$Pu_2(C_2O_4)_3$ (742)	752	741	300–350

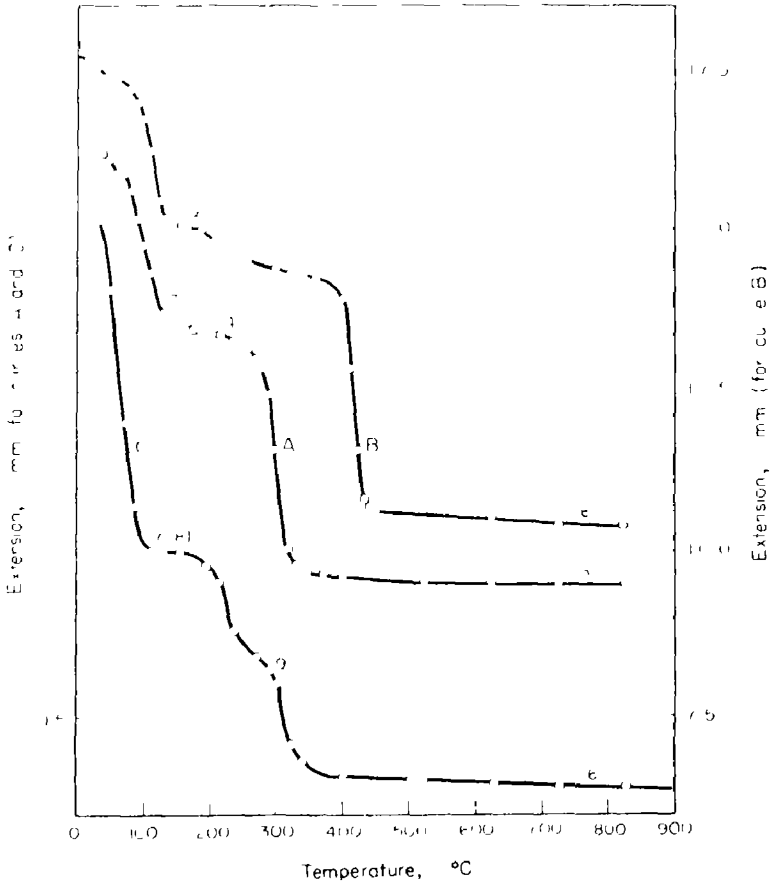


FIG. 1—Thermogravimetry of plutonium oxalates A—Pu(III) Oxalate in Air B—Pu(III) Oxalate in argon C—Pu(IV) Oxalate in air 1 $Pu_2(C_2O_4)_3 \cdot 10H_2O$, 2 $Pu_2(C_2O_4)_3 \cdot 9H_2O$, 3 $Pu_2(C_2O_4)_3 \cdot 2H_2O$, 4 $Pu_2(C_2O_4)_3 \cdot H_2O$, 5 $Pu_2(C_2O_4)_3$, 6 PuO_2, 7 $Pu(C_2O_4)_2$, 8 $Pu(C_2O_4)_2 \cdot H_2O$, 9 $Pu(C_2O_4)(CO_3)_{0.5}$

Thermal decomposition For studying the thermal decomposition, approximately 10 mg of the oxalates were loaded into a silica spring thermobalance with a sensitivity of 2 5 mm/mg and the temperature raised at a rate of 5°C/min The weight changes were observed with an index fibre and a cathetometer which could be read to ± 0 01 mm Tables 1 and 2 and Fig 1 show the intermediate products formed during the thermal decomposition of plutonium (IV) and plutonium (III) oxalates

Analysis of the intermediate product A sample of plutonium(IV) oxalate was heated to 250 C in the thermobalance, cooled rapidly and the intermediate product analysed Carbonate was determined using a CONWAY diffusion cell(5) containing sulphuric acid and barium hydroxide Plutonium was estimated by alpha counting and oxalate by permanganate titration The percentage of plutonium in the trivalent state was also approximately determined to be greater than 75 per cent by titration with standard ceric sulphate solution from an agla micro-syringe using ferrous-o-phenanthroline as indicator Table 3 gives the results of this analysis

TABLE 3 ANALYSIS OF THE INTERMEDIATE PRODUCT

Run	Weight of substance	Percentage obtained of			Molar ratio		
		CO_3^{2}	$C_2O_4^{2}$	Pu	CO_3^{2}	$C_2O_4^{-}$	Pu
1	12 06 mg	8 86	25 9	66 2	1	1 99	1 88
2	9 42 mg	8 32	24 6	64 5	1	2 01	1 90
Theoretical for $Pu(C_2O_4)(CO_3)_{0\ 5}$		8 40	24 7	66 9	1	2	2

Radiochemistry and Isotope Division
Atomic Energy Establishment Trombay
Bombay-73, India

G S RAO
M S SUBRAMANIAN
G A WELCH

(5) E J CONWAY, *Microdiffusion Analysis and Volumetric Error*, Crosby-Lockwood, London (1947)

The crystal structure of calcium bromide

(*Received* 6 *May* 1963)

THE CRYSTAL structure of calcium bromide has been studied by DOLL and KLEMM (1) These authors report the structure to be isomorphous with that of $CaCl_2$ crystallizing in the orthorhombic space group D_{2h}^{12}-Pnnm with cell constants a 6 55 Å, b 6 88 Å and c = 4 34 Å However no attempt was made to determine the detailed structural parameters As part of a programme to study the crystal energy of alkaline earth compounds, this paper reports a determination of these parameters by the use of powder X-ray diffraction techniques Anhydrous $CaBr_2$ was prepared by heating the commercially available dihydrate to 250 C under vacuum for a period of 2 hr Powder diffraction data was obtained under anhydrous conditions using an automatic recording diffractometer equipped with a geiger counter detector CuK_α radiation (λ_{α_1} 1 5405 Å) was used and the spectra were calibrated against the known spectrum of α-quartz (a 4 913 Å, c = 5 405 Å) The unit cell dimensions obtained are

a 6 584 ± 0 006 Å
b = 6 871 ± 0 006 Å
c 4 342 ± 0 004 Å

These values are in reasonable agreement with those of DOLL and KLEMM

The data were collected to a maximum value for [(sin θ) λ] of 0 40 Å⁻¹ Twenty-two reflections were observed to be completely resolved The intensities of these peaks were estimated from a measure of their half width and peak heights and reduced to relative scattering factor magnitudes in the usual manner. These scattering factors were then used in a least squares calculation minimizing the sum of the weighted squares of the difference between observed and calculated scattering factors with respect to the changes in those positional parameters not fixed by symmetry. The calcium ion was placed in the special positions 2a (000, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$) of space group Pnnm and the bromide ions in positions 4g ($x, y, 0$; $\bar{x}, \bar{y}, 0$; $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}$; $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}$). The trial values of the bromine parameters were $x = 0.275$ and $y = 0.325$, the reported chlorine parameters in $CaCl_2$.⁽²⁾ An overall thermal vibration parameter B was restricted to a value of 1.0 Å². The ratio of observational equations to parameters in the least squares calculation was thus equal to eleven. Five least squares iterations were carried out. After the third cycle, the indicated changes in the parameters were less than 5×10^{-5}. The final value of the reliability index $R = \Sigma \| F_0 | - | F_c \| / \Sigma | F_0 |$ was 0.102. The resulting values for the bromine positional parameters with their respective standard deviations estimated from the least square normal equation matrix are

---

(1) W DOLL and W KLEMM, *Z anorg Chem* **241**, 239 (1939)

$$x = 0.2636 \pm 0.0029$$
$$y = 0.3417 \pm 0.0026$$

In the resulting structure the calcium ion is surrounded by six nearest bromide ions in a distorted octahedral configuration with four Ca-Br distances of 2.88 Å and two of 2.91 Å in accord with the sum of the accepted ionic radii of 2.94 Å. The various Br-Ca-Br angles range from 82°21′ to 97°39′ with an average value of 90° demanded by the crystal symmetry. The nearest bromine-bromine approach is 3.79 Å and is also consistent with an ionic structure.

Acknowledgments. This work was supported by a grant from the National Aeronautics and Space Administration. The computational facilities used are supported by the Atomic Energy Commission grant number AT-(40-1)-1825.

Department of Chemistry
Rice University
Houston, Texas, U.S.A.

F. B. BRACKETT
T. E. BRACKETT
R. L. SASS

⁽²⁾ A. K. VAN BEVER and W. NIEUWENKAMP, *Z. Krist.* **90**, 374 (1935).

The formation of mercury derivatives in reactions involving sodium derivatives of metal carbonyls prepared from sodium amalgam

(*Received* 24 *April* 1963)

RECENTLY we have been investigating the reactions of certain sodium derivatives of metal carbonyls with various organic halides⁽¹,²,³⁾ in order to prepare new organometallic compounds. The sodium derivatives required for this work have been obtained by cleaving certain binuclear carbonyls with dilute sodium amalgam. We now wish to report several cases where the mercury from the sodium amalgam has entered into the reaction to form the corresponding mercury derivative of the metal carbonyl. A similar reaction has been recently reported⁽⁴⁾ where dicobalt octacarbonyl formed $Hg[Co(CO)_4]_2$ on reaction with dilute sodium amalgam in a non-polar solvent such as hexane.

Experimental

The sodium derivatives $NaMn(CO)_5$, $NaFe(CO)_2C_5H_5$, and $NaCo(CO)_4$ were prepared from the reactions of $Mn_2(CO)_{10}$, $[C_5H_5Fe(CO)_2]_2$, and $Co_2(CO)_8$, respectively, with ~1% sodium amalgam in tetrahydrofuran (redistilled over lithium aluminum hydride).⁽¹,²,³⁾ One sample of each of the mercury derivatives was identified by analyses for carbon, hydrogen, mercury, and the transition metal

---

⁽¹⁾ R. B. KING, *J. Amer. Chem. Soc.* **85**, 1922 (1963).
⁽²⁾ R. B. KING, *J. Amer. Chem. Soc.* **85**, 1918 (1963).
⁽³⁾ R. B. KING, *Inorg. Chem.* **2**, 531 (1963).
⁽⁴⁾ S. V. DIGHE and M. ORCHIN, *Inorg. Chem.* **1**, 965 (1962).

HNO_3 are analogous to the spectrum of DEHPA, the very weak absorption assigned to the nitrate group[13,14] at 1300 cm^{-1} appears in 3 M acid, becoming slightly stronger in 6 M acid. The OH stretching band in the region 2680–2350 cm^{-1} persists in the extraction of 6.0 M nitric acid solution: it has been pointed out by PEPPARD *et al.*[14] that even if the dimer of DEHPA is broken, new bonds formed with the nitric acid hydrogen would give rise to a bonded OH absorption in approximately the same region.

In the extraction of uranyl nitrate solution (5 *g/l*) the intensity of the band at 930 cm^{-1}, which is assigned to the uranyl group[15] decreases with increasing acidity below 3 M, and then increases again in 6 M acid. Simultaneously the intensities of the OH stretching and bending bands decrease, while the P → O absorption band at 1230 cm^{-1} shifts as follows: 1205 cm^{-1} (0.15 M HNO_3), 1210 cm^{-1} (1.0 M HNO_3), 1215 cm^{-1} (3.0 M HNO_3), 1210 cm^{-1} (6.0 M HNO_3). These results correspond to the changes shown in Fig. 1.

At an aqueous concentration of 25 g/l uranyl nitrate (Fig. 5) the uranyl band at 930 cm^{-1} is sharper than that for 5 g/l because of the increased organic phase uranium concentration. At the same time, the OH stretching and bending bands almost disappear, and the P → O frequency at 1230 cm^{-1} shifts as follows: 1135 cm^{-1} (0.15 M HNO_3), 1140 cm^{-1} (1.0 M HNO_3), 1155 cm^{-1} (3.0 M HNO_3), 1140 cm^{-1} (6.0 M HNO_3). Furthermore the absorptions at 1085 and 1060 cm^{-1} observed in the extraction of UO_2SO_4 which have uncertain assignments,[1] appear in addition to the [P—O]—C stretching vibration at 1030 cm^{-1} in 0.15, 1.0 and 6.0 M nitric acid concentrations. In addition the band at 1260 cm^{-1} which is assigned to the NO_2 symmetric stretching vibration[16,17] appears in 3 M acid and more strongly in 6 M acid. This suggests that the extraction of uranium by DEHPA at 3 M acid may be represented by Equation (8).

The above results show that the P → O absorption band at 1230 cm^{-1} is shifted to lower frequencies by the formation of the uranium–DEHPA complex independently of the aqueous nitric acid concentration, confirming that the uranium extracted into DEHPA solution by either cation-exchange or by solvation is bonded to the phosphoryl oxygen atom.

Acknowledgements—The author wishes to thank Mr. T. Goto of our Institute for assistance with experimental work and Atomic Fuel Corporation for a gift of di-(2-ethylhexyl)-phosphoric acid.

---

[13] R. A. MARCUS and J. M. FRESCO, *J. Chem. Phys.* **27**, 564 (1957).
[14] D. F. PEPPARD and J. R. FERRARO, *J. Inorg. Nucl. Chem.* **15**, 365 (1960).
[15] E.g. B. M. GATEHOUSE and A. E. COMYNS *J. Chem. Soc.* 3965 (1958); G. L. CALDOW, A. B. VAN CLEAVE and R. L. EAGER *Canad. J. Chem.* **38**, 772 (1960).
[16] D. F. PEPPARD and J. R. FERRARO *J. Inorg. Nucl. Chem.* **10**, 275 (1959).
[17] C. J. HARDY and D. SCARGILL, *J. Inorg. Nucl. Chem.* **17**, 337 (1961).

Additional samples of the mercury compounds were identified by comparison of infrared spectra, n.m.r. spectra (in the case of $[C_5H_5Fe(CO)_2]_2Hg$), and behavior on chromatography or sublimation with this authentic sample. Analyses were performed by Dr. A. Bernhardt, Mikroanalytisches Laboratorium, Max-Planck-Institut fur Kohlenforschung, Mulheim (Ruhr), Germany.

Formation of $Hg[Mn(CO)_5]_2$. The analysed sample was obtained by refluxing ~25 mmoles of $NaMn(CO)_5$ prepared from sodium amalgam with ~12.5 mmoles of 1,4-dibromobutane in 100 ml of tetrahydrofuran for 2 hr. Solvent was removed and the residue extracted with dichloromethane. The residue from the dichloromethane extraction was sublimed at 100–140°/0.1 mm to give 0.85 g (11.5 per cent yield based on $Mn_2(CO)_{10}$) of pale yellow crystals of $Hg[Mn(CO)_5]_2$, dec. ~155°, which was purified by a second sublimation.

Analysis. Calc. for $C_{10}O_{10}Mn_2Hg$: C, 20.3; H, 0.0; Mn, 18.6; Hg, 34.0%. Found: C, 20.4; H, 0.0; Mn, 18.8; Hg, 33.6%.

The formation of $Hg[Mn(CO)_5]_2$ was also observed in the reactions of $NaMn(CO)_5$ with 2-chlorotropone and with the acid chloride of cyclopropanecarboxylic acid. The $Hg[Mn(CO)_5]_2$ obtained in these reactions was identical with a sample obtained from $NaMn(CO)_5$ and $Hg(CN)_2$.(5)

Formation of $Hg[Fe(CO)_2C_5H_5]_2$. The analysed sample was obtained from 100 mmoles of $NaFe(CO)_2C_5H_5$ prepared from sodium amalgam and ~50 mmoles of succinyl dichloride in 300 ml of tetrahydrofuran. The product was isolated by extraction of the evaporated reaction mixture with dichloromethane. After evaporating this dichloromethane extract at reduced pressure the residue was chromatographed in benzene solution on a 6 × 50 cm alumina column. A yellow-orange band of $Hg[Fe(CO)_2C_5H_5]_2$ immediately followed by a red-brown band of $[C_5H_5Fe(CO)_2]_2$ was observed. The mercury derivative was isolated by evaporation of the eluate from the yellow-orange band and recrystallization of the residue from a mixture of dichloromethane and hexane to give 0.71 g (2.6 per cent yield based on $[C_5H_5Fe(CO)_2]_2$) of orange $Hg[Fe(CO)_2C_5H_5]_2$,(6) m.p. 145–146°.

Analysis. Calc. for $C_{14}H_{10}Fe_2O_4Hg$: C, 30.2; H, 1.8; Fe, 20.2; Hg, 36.2%. Found: C, 30.7; H, 1.8; Fe, 20.2; Hg, 35.8%.

The proton n.m.r. spectrum of $Hg[Fe(CO)_2C_5H_5]_2$ was characterized by a single sharp peak at $\tau = 5.27$ due to the ten cyclopentadienyl protons.

The formation of $Hg[Fe(CO)_2C_5H_5]_2$ was also observed in the reactions of $NaFe(CO)_2C_5H_5$ with perfluoroglutaryl dichloride(2) and with $(C_5H_5)_2MCl_2$ ($M = Ti$ and Zr). The $Hg[Fe(CO)_2C_5H_5]_2$, obtained in these reactions was identical with a sample, m.p. 142–144°, obtained from $Hg(CN)_2$ and $NaFe(CO)_2C_5H_5$.(6)

Formation of $Hg[Co(CO)_4]_2$. The analysed sample was obtained from ~30 mmoles of $NaCo(CO)_4$ prepared from sodium amalgam and 15 mmoles of perfluoroglutaryl dichloride in 100 ml of redistilled tetrahydrofuran. After removal of solvent at reduced pressure the residue was extracted with dichloromethane. Solvent was removed from the filtered dichloromethane extracts at reduced pressure and the product recrystallized from pentane to give 0.55 g (6.7 per cent yield based on $Co_2(CO)_8$) of pale orange crystals of $Hg[Co(CO)_4]_2$ which were purified further by two sublimations at 60°/0.1 mm.

Analysis. Calc. for $C_8O_8Co_2Hg$: C, 17.7; H, 0.0; Co, 21.7; Hg, 37.0%. Found: C, 17.8; H, 0.0; Co, 21.5; Hg, 36.8%.

The formation of $Hg[Co(CO)_4]_2$ was also observed in the reactions of $NaCo(CO)_4$ with hexachloropropene and with acrylyl chloride. The $Hg[Co(CO)_4]_2$ obtained in these reactions was identical with a sample prepared from cobalt (II) nitrate, sodium dithionite, ammonia, mercury (II) cyanide, and carbon monoxide.(7)

Discussion

The tendency for the mercury of the sodium amalgam to form mercury derivatives of metal carbonyls in the reactions described above is an important disadvantage of the sodium amalgam route for the preparation of sodium derivatives of metal carbonyls since in some cases contamination of other products of interest obtained from these reactions with these mercury derivatives occurs.

Of the three mercury derivatives discussed in this paper $Hg[Mn(CO)_5]_2$ is the least likely to be a troublesome contaminant in organometallic compounds prepared from the corresponding sodium salt. The solubility of $Hg[Mn(CO)_5]_2$ is so low in dichloromethane, a useful solvent for dissolving out organomanganese compounds from the residues from a reaction mixture, that significant quantities are not extracted out with the organomanganese compounds. It only presents a problem when a product is sublimed directly from a dried reaction mixture without any intervening extraction steps. Incidentally, the volatility of $Hg[Mn(CO)_5]_2$ at $\sim 100°/0.1$ mm, although not surprising in view of the volatility of related compounds such as $Hg[Co(CO)_4]_2$, does not seem to have been described previously.

---

(5) W. Hieber and W. Schropp, Jr., *Ber.* **93**, 455 (1960).

(6) E. O. Fischer and R. Bottcher, *Z. Naturf.* **10b**, 600 (1955).

(7) W. Hieber, E. O. Fischer and E. Bockly, *Z. anorg. Chem.* **269**, 308 (1952).

The potential contamination problems from $Hg[Fe(CO)_2C_5H_5]_2$ and $Hg[Co(CO)_4]_2$ produced in these reactions are somewhat greater. The iron derivative $Hg[Fe(CO)_2C_5H_5]_2$ is best removed from other organoiron compounds by chromatography on alumina in benzene solution or by sublimation of a desired volatile product away from the nonvolatile $Hg[Fe(CO)_2C_5H_5]_2$. The cobalt derivative $Hg[Co(CO)_4]_2$ is probably best removed from other cobalt compounds by fractional sublimation.

It is also to be noted that solutions of lithium derivatives of metal carbonyls in tetrahydrofuran can be prepared from a solution of the binuclear carbonyl derivative such as $Co_2(CO)_8$ or $Mn_2(CO)_{10}$ in tetrahydrofuran and lithium wire.[8] This method eliminates entirely the use of mercury and the concomitant danger of the formation of mercury derivatives.

Note added in proof. Since this note was submitted a report has appeared by GREEN and NAGY[9] noting the formation of small amounts of $[C_5H_5Fe(CO)_2]_2Hg$ in the reaction between allyl chloride and $NaFe(CO)_2C_5H_5$ prepared with sodium amalgam.

Acknowledgment. The author is indebted to Mr. M. BISNETTE for experimental assistance and to Dr. F. B. BROWN of Union Carbide Olefins, Co., South Charleston, West Virginia, for a generous gift of dicobalt octacarbonyl.

R. B. KING

Mellon Institute
4400, *Fifth Avenue*
Pittsburgh 13, *Pennsylvania*

[8] W. R. McCLELLAN, *J. Amer. Chem. Soc.* **83**, 1598 (1960).

[9] M. L. H. GREEN and P. L. I. NAGY, *J. Chem. Soc.* 189 (1963).

Detection of ^{146}Pm among the products of uranium fission

(*Received* 22 *March* 1963, *in revised form* 14 *May* 1963)

WHILE the shielding requirements of 2.67 *y* ^{147}Pm were recently being investigated in our laboratory gamma activities at 0.45 and 0.75 MeV were observed in about equal amounts. Although these gammas are in very low abundance relative to ^{147}Pm, they might constitute an appreciable shielding problem with very large (Mc range) promethium sources. The gammas were identified as being from 1.94 *y* ^{146}Pm, which has been prepared by (p, n) and $(p, 3n)$ reactions[1] but has not previously been reported among the products of fission reactions. For the first few years after reactor discharge the radiation from ^{146}Pm is masked by the gammas from 42 *d* ^{148}Pm, and even after the ^{148}Pm has decayed away the low abundance of ^{146}Pm makes detection difficult.

The amount of ^{146}Pm formed in nuclear reactors is determined by three different neutron reactions. One reaction is the production of ^{146}Pm as a direct fission product. The fisson yield values predicted by the methods of GRUMMITT and MILTON[2], WAHL[3], STEINBERG and GLENDENIN[4], and PAPPAS[5] are 2×10^{-6}, 8×10^{-7}, 1.2×10^{-7}, and about 10^{-8} respectively for the fractional chain yield. A second reaction is the formation from ^{147}Pm by a $(n, 2n)$ reaction. The threshold energy for this

[1] E. G. FUNK Jr., J. W. MIHELICH and C. F. SCHWERDTFEGER, *Phys. Rev.* **120**, 1781 (1960).

[2] W. E. GRUMMITT and G. M. MILTON, Report CRC 694 (AECL 454) (May, 1957).

[3] A. C. WAHL, *J. Inorg. Nucl. Chem.* **6**, 263 (1958).

[4] E. P. STEINBERG and L. E. GLENDENIN, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, Vol. 7, p. 3 (1955).

[5] A. C. PAPPAS, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, Vol. 7, p. 19 (1955).

reaction according to EVERLING *et al* (6) is 7 0 ± 0 1 MeV, but they give the beta decay energy as only 0 75 MeV compared with the experimentally determined value of 1 53 MeV(1) A value of 7 8 MeV was therefore used for the threshold energy to correct for the apparently low mass of ^{146}Pm as given by EVERLING According to ROY and HAWTON(7), this energy corresponds to a cross section for fission neutrons of 5 9 mbarns for the ^{147}Pm (n, $2n$) reaction, with an expected accuracy of a factor of two or three The third reaction is the capture of neutrons by ^{145}Pm No predicted values for this reaction are available

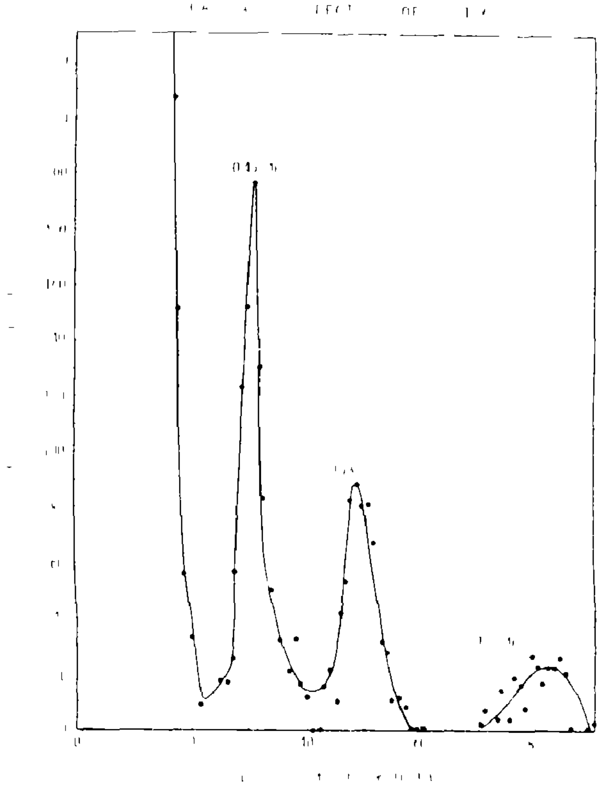


FIG 1

The initial observation of ^{146}Pm was made while counting promethium obtained from Oak Ridge The total beta activity of the purified promethium was determined using a beta proportional counter of known efficiency for ^{147}Pm (calibrated by 4π beta counting) The gamma activity was measured by means of a 5-in NaI (Tl) crystal provided with anti-coincidence shielding(8) and a Model 3412 RIDL 400-channel analyser Sources containing about 1 mc of ^{147}Pm were counted for 30 min To reduce the bremsstrahlung count rate, the source was surrounded with about 0 14 g cm^2 of lead The 0 45 and 0 75 MeV photopeaks of ^{146}Pm were well resolved from each other and from the bremsstrahlung originating from the 0 225 MeV beta of ^{147}Pm, as shown in the accompanying figure The number of photons per minute at the two energies were determined from the known detector efficiencies and corrected for background and the observed sum peak at 1 20 MeV The results are summarized below

^{147}Pm activity, β/m		3 43	10^{9}	3 %
Gamma activity, γ/m,	0 45 MeV	1036	100	
	0 75 MeV	901	90	
Gammas per Beta,	0 45 MeV	3 02	10^{-7}	
	0 75 MeV	2 63	10^{-7}	

(6) F EVERLING, L A KONIG, J H E MATTAUCH and A H WAPSTRA *Nucl Phys* **18**, 529 (1960)

(7) J C ROY and J J HAWTON, Report CRC-1003 (December 1960)

(8) R W PERKINS, J M NIELSEN and R N DIEBEL, *Rev Sci Instrum* **31**, 1344 (1960)

To determine whether a similar amount of ^{146}Pm was formed under different reactor conditions, a sample of aged mixed fission products available at Hanford was also investigated. The rare earths were separated from the fission product mixture by a neodymium fluoride carrier precipitation. The promethium was then isolated by ion exchange, using a modified EDTA elution technique(9, 10, 11). The feed with added neodymium and samarium was absorbed on a 1.87 cm^2 × 20 cm bed of Dowex 50W-X8 (50–100 mesh). A second bed of the same resin (0.775 cm^2 × 100 cm) was saturated with yttrium. The columns were eluted in series at 58°C and 0.7 ml min^{-1} flow rate, using 0.015 *M* EDTA buffered to pH 8.6 with ammonium hydroxide. Samarium and neodymium separated into individual bands behind the yttrium barrier, with the promethium concentrated between them. The promethium fraction contained no detectable radioactive impurities. The amount of Pm^{146} observed in this sample was similar to the amount found in the Oak Ridge material.

Since ^{146}Pm decays faster than ^{147}Pm (1.94 ± 0.19 *y* compared with 2.67 *y*), the observed gamma per beta values need to be corrected for cooling time to obtain the amount at reactor discharge. The promethium obtained from Oak Ridge had been recovered from Brookhaven reactor wastes, and at the time of our measurements it had been cooled about 8 years after reactor discharge.(12) The activity at reactor discharge was therefore 1.23 × 10^{-6} total gammas from ^{146}Pm per beta from ^{147}Pm. Using a value of 1.30 gammas per ^{146}Pm decay the ratio at reactor discharge of ^{146}Pm atoms to ^{147}Pm atoms was found to be 6.9 × 10^{-7}.

The irradiation conditions in the Brookhaven reactor vary considerably, and the exact conditions for production of the promethium used in this work are not known. However, since the quantity being measured is the ratio of nuclides of similar half-life, the uncertainty in reactor conditions has only a minor effect on the results. According to Chastain(13), natural uranium fuel in the Brookhaven reactor is irradiated to a 10–20 per cent burnup of the ^{235}U at a thermal flux of about 5 × 10^{12} neutrons/cm^2 sec, with the fast flux being about 10 per cent of the thermal flux. This corresponds to irradiation for about 1.6 years, with the integrated thermal flux (nvt) being 2.6 × 10^{20}. For these conditions the ratio of atoms of ^{146}Pm to ^{147}Pm produced by the (*n*, 2*n*) route is only about 6.9 × 10^{-8} if the neutron capture cross section of ^{146}Pm is small, and even lower if the ^{146}Pm cross section is large. Therefore, over 90 per cent of the ^{146}Pm is probably produced by direct fission yield.

If the ^{146}Pm neutron capture cross section is small, the yield of ^{146}Pm is 4.2 ± 1.2 × 10^{-7} of the chain yield. The major source of uncertainty in this value is from the (*n*, 2*n*) cross section. A yield of 8 × 10^{-7} as predicted according to Wahl would require a ^{146}Pm neutron capture cross section of about 10,000 barns, while a yield of 2 × 10^{-6} as predicted according to Grummitt and Milton would require a ^{146}Pm neutron capture cross section of about 30,000 barns. Since the fractional chain yield is over 3 × 10^{-7}, the predicted value according to Pappas is very low, and the value according to Steinberg and Glendenin is at least slightly low. The accuracy of the other two values is not known since the neutron capture cross section of ^{146}Pm is not known. Quite similar conclusions were obtained using the data from the Hanford material even though the reactor conditions were not the same.

Fission Product Chemistry
Chemical Research Operation
General Electric Company,
Richland, Washington, U.S.A.

F. P. Roberts
E. J. Wheelwright
H. H. van Tuyl*

---

* General Electric Company, Richland, Washington. Work performed under Contract No. AT(45-1)-1350 for the U.S. Atomic Energy Commission.

(9) F. H. Spedding, J. E. Powell and E. J. Wheelwright, *J. Amer. Chem. Soc.* **76**, 2557 (1954).

(10) D. B. James, J. E. Powell and F. H. Spedding, *J. Inorg. Nucl. Chem.* **19**, 133 (1961).

(11) L. A. Bray, L. F. Lust, R. L. Moore, F. P. Roberts, F. M. Smith, H. H. Van Tuyl and E. J. Wheelwright, Report HW-70998 (September 1961).

(12) T. A. Butler and R. W. Schaich, Private Communication (February, 1963).

(13) J. W. Chastain Jr., *U.S. Research Reactor Operation and Use*, Addison-Wesley, Reading, Mass. (1958).

J. Inorg. Nucl. Chem. 1963, Vol. 25, p. 1301. Pergamon Press Ltd. Printed in Northern Ireland

LETTER TO THE EDITORS

A method of purification of protactinium from niobium

(*Received* 31 *May* 1963)

A stock of 125 g of protactinium-231 was recently purified at Windscale and Harwell(1, 2) and at that time spectrographic analysis of the product indicated a total impurity content of 0.3 per cent for the impurities detected. However, the presence of niobium lines was overlooked in the very complex spectrum of protactinium and improvements in spectrographic analysis techniques have now shown that this material contains about 4 per cent of niobium. Niobium is very similar to protactinium in chemical properties and had followed it through many purification stages involving solvent extraction and ion exchange. Grosse(3) finally purified the protactinium he used for atomic weight determination in 1934 by precipitating it as peroxide from sulphuric acid, leaving zirconium, hafnium, tantalum and niobium in solution. Casey and Maddock(4) have used a peroxide precipitation stage in their purification method.

We have now used this method to obtain about 500 mg of protactinium containing < 0.02 per cent of niobium. The protactinium was precipitated from 8 N HCl/0.5M HF as hydroxide and then dissolved in 40 ml of 40% sulphuric acid. The container was packed around with ice and 20 ml of 100 vol. hydrogen peroxide added, followed by enough ammonia to make the solution just alkaline to litmus. After 2 hr standing the yellow peroxide precipitate was centrifuged off, washed twice with water and dissolved in cold, 40% sulphuric acid.

Spectrographic analysis showed that about 0.3 per cent of niobium was still present, so the peroxide precipitation was repeated. In the final solution the following impurities were found:

Fe	Mg	Al	Cu	Nb
600	10	100	50	< 200 p.p.m.

There is rather more iron than reported on the original solution(1, 2) but this had probably been introduced during our early experiments. The detection limit of the special method developed for niobium(5) is 200 p.p.m. About 80 per cent of the original material was obtained in this pure form; quantitative precipitation was not attempted since residues could be combined with a later batch.

Spectrographic analysis is rather insensitive for the detection of uranium but a determination of uranium on a specimen of the 125 g stock at Oak Ridge National Laboratory by the isotope dilution technique has given a result of 7 p.p.m.(6)

Acknowledgement—The spectrographic analyses were carried out by F. T. Birks, A. M. Thomas and G. J. Weldrick.

A. J. Walter

Chemistry Division
U.K.A.E.A. Research Group
Atomic Energy Research Establishment
Harwell

(1) D. A. Collins, J. J. Hilary, J. S. Nairn and G. M. Phillips, *J. Inorg. Nucl. Chem.* **24**, 441 (1962).
(2) N. Jackson, F. J. G. Rogers and J. Short, AERE R-3311 (1960).
(3) A. V. Grosse, *Proc. Roy. Soc.* **150**, 363 (1935).
(4) A. T. Casey and A. G. Maddock, *J. Inorg. Nucl. Chem.* **10**, 58 (1959).
(5) F. T. Birks, To be published (1963).
(6) Progress report ORNL-3314 (page 160).

J. Inorg. Nucl. Chem. 1963, Vol. 25, pp. 1303 to 1319. Pergamon Press Ltd. Printed in Northern Ireland

ALPHA DECAY OF NEUTRON-DEFICIENT ASTATINE ISOTOPES

R. W. Hoff, F. Asaro and I. Perlman
Lawrence Radiation Laboratory, University of California
Livermore and Berkeley, California

(*Received* 3 *April* 1963)

Abstract—The α-particle and γ-ray spectra of neutron-deficient isotopes of astatine were studied with a magnetic α-particle spectrograph and α–γ coincidence apparatus. A new α-emitting isotope, ^{202}At, was identified, as were new isomers of ^{204}At and ^{206}At. Results are tabulated below.

Mass no.	E_α(MeV)	Half-life (min)
^{201}At	6.342 ± 0.006	1.5 ± 0.1
^{202}At	6.227 ± 0.003 (36 ± 2%)	3.0 ± 0.2
^{202}At	6.133 ± 0.002 (64 ± 2%)	
^{203}At	6.085 ± 0.001	7.4 ± 0.3
^{204}At	5.948 ± 0.003	9.3 ± 0.2
^{205}At	5.896 ± 0.004	26.2 ± 0.5
^{206}At	5.696 ± 0.008	31.0 ± 1.5
^{207}At	5.752 ± 0.008	1.4 hr

Alpha groups with energies of 6.412 ± 0.009 and 6.465 ± 0.011 MeV (relative intensities about 60 and 40 per cent respectively) and an overall half-life of 0.9 ± 0.2 min are tentatively assigned to ^{200}At. α–γ coincidence measurements have shown a 68 keV photon to be in coincidence with the 5.696 MeV ^{206}At α-particles. Upper limits were set for photons in coincidence with the other α-groups studied. No evidence was found for the α-decay of the 25 min ^{204}At and 2.9 hr ^{206}At electron-capture activities which have been studied earlier by other workers.

The decade following 1940 witnessed the preparation of a large number of new α-emitters covering a span of elements from bismuth to new elements well into the transuranium region. Perlman *et al.*⁽¹⁾ showed that the decay properties of these new alpha emitters could be correlated with those of previously known α-emitters and that systematic trends existed which could be employed in predicting properties. Later correlations,⁽²⁾ which included new information for α-emitters obtained during the past decade, have extended these systematics to the α-decay of the heaviest known elements and have enabled meaningful predictions to be made for the decay of nuclides even heavier than those known today. One of the most useful regularities for predicting decay properties is the relation between α-energy and the mass number. Alpha decay energy increases regularly with decreasing neutron number for a given element in the region $N > 128$. Thus, a family of nearly straight parallel lines are formed by joining points for isotopes of each element. A sharp discontinuity in this correlation occurs at $N = 127$ due to the increased stability at the major closed shell of 126 neutrons The alpha decay energies decrease sharply and reach a minimum at 125 neutrons There then follows another region of regularly increasing α-energy below the closed shell The astatine isotopes investigated in our work lie in this region just below the 126-neutron closed shell The preliminary results were reported in an earlier publication (3)

---

* Work performed under the auspices of the U.S. Atomic Energy Commission.

(1) I. Perlman, A. Ghiorso and G. T. Seaborg, *Phys. Rev.* 77, 26 (1950).

(2) R. A. Glass, S. G. Thompson and G. T. Seaborg, *J. Inorg. Nucl. Chem.* 1, 3 (1955); B. M. Foreman and G. T. Seaborg, *Ibid.* 7, 305 (1958).

Among the difficulties in studying these nuclides are that they cannot be produced singly, and the half-lives are rather short for rigorous chemical separation and detailed measurement of decay properties It should also be borne in mind that all are unstable with respect to electron capture

The original study of the decay of neutron-deficient astatine isotopes was performed by BARTON *et al* (4) They produced astatine isotopes in the mass number range 201 209 by irradiating bismuth with high-energy helium ions Particular emphasis was placed upon characterizing half-lives and α-particle energies, for which they used an ionization chamber connected to a multichannel pulse-height analyser Mass number assignments for ^{201}At–^{209}At were made by chemically separating and identifying electron-capture (or positron) decay products of lower atomic number In some instances, relative yields for the production of specific isotopes as a function of bombarding helium-ion energy served to aid in the assignment of mass number Later work by STONER(5) yielded more detailed information for the decay of astatine isotopes with mass numbers 206 209

In the past few years heavy ions have been introduced as projectiles for the production of neutron-deficient isotopes The irradiation of most targets with heavy projectiles such as carbon or nitrogen ions will produce excited compound nuclei in themselves neutron-deficient and which de-excite by boiling off several more neutrons BURCHAM(6) and STONER(5) studied light astatine isotopes produced in the bombardment of gold and platinum targets with carbon and nitrogen ions In particular, they observed the α-decay of ^{203}At, ^{205}At and ^{207}At and confirmed the results of BARTON *et al* (4) A paper by FORSLING *et al* (7) describes the results of a study of astatine isotopes produced in bombardments of gold targets with cyclotron-accelerated carbon and neon ions Following chemical purification, the astatine fractions were analyzed by use of an electromagnetic isotope separator After isotope separation the alpha decay of astatine isotopes with mass numbers 202-207 was measured in an ionization chamber-pulse analyzer combination These results of FORSLING *et al* are in general agreement with our data

A recent investigation by LATIMER *et al* (8) of α-particle branching ratios for $^{202-206}$At in which the astatine isotopes were produced with heavy ion projectiles yielded decay properties for these isotopes in agreement with our results THOMAS *et al* (9) have measured complete excitation functions for the production of $^{201-208}$At with carbon and nitrogen ion projectiles on targets of gold and separated platinum isotopes These excitation functions, along with the isotope separation studies of FORSLING *et al*,(7) provide the most conclusive supporting evidence for the mass assignments which were made in our original publication(3) and which were based upon experimental evidence to be described in this paper

---

(3) R W HOFF, F ASARO and J PERLMAN, *Bull Amer Phys Soc* Ser II, **44**, 293 (1959)

(4) G W BARTON, A GHIORSO, and I PERLMAN, *Phys Rev* **82**, 13 (1951)

(5) A W STONER, Report UCRL-3471 (1956)

(6) W E BURCHAM and B C HAYWOOD, *Proc Phys Soc* (London) **69** A, 862 (1956), W E BURCH *Ibid* **67** A, 555 (1954), W E BURCHAM, *Ibid* **67** A, 733 (1954)

(7) W FORSLING, T ALVAGER, L W HOLM, O MELIN, J UHLER and B ÅSTROM, *Arkiv Fysik* **19** 83 (1961)

(8) R M LATIMER, G E GORDON and T D THOMAS, *J Inorg Nucl Chem* **17,** 1 (1961)

(9) T D THOMAS, G E GORDON, R M LATIMER and G T SEABORG, *Phys Rev* **126,** 1805 (196

The present investigation is confined to the alpha decay of the astatine isotopes (mass numbers 200–207) produced in appreciable quantities in irradiations of gold targets with carbon and nitrogen ions in the Heavy Ion Linear Accelerator (Hilac) at Berkeley The use of heavy ion projectiles in the production and study of light astatine isotopes is advantageous because interference from heavier isotopes (A 207) is reduced relative to the situation with helium ion irradiations of bismuth The formation of lighter products is favoured for two reasons First, the compound nucleus is lighter for carbon ion bombardments of gold (^{209*}At) as opposed to that for helium ion bombardments of bismuth (^{213*}At), and second, the high Coulomb barrier for carbon ions eliminates low nuclear excitation of the compound nucleus, even when thick targets are employed

In the present study the high intensities of carbon and nitrogen ions available in the Hilac made it possible to prepare samples strong enough for α-particle analysis using a magnetic α-particle spectrograph (10) The energy resolution was several-fold better than that possible with ionization chambers, therefore it was easier to resolve the several components present in each sample

EXPERIMENTAL METHODS AND RESULTS

A *Target preparation bombardment, and chemistry*

The target consisted of a gold foil in front of which there was usually interposed an aluminium absorber foil By using different thicknesses of aluminium as well as gold it was possible to control the energy band to which the target atoms were exposed and in this way to change the ratios of the several astatine isotopes produced This selectivity although crude, was sufficient to make mass number assignments The information so obtained is shown in Table 1 and will be discussed below

The carbon ion beam intensities were in the range of 1–2 micro-amperes The target and absorber foils were cooled with streams of helium gas which had been precooled by flowing through a coil immersed in liquid nitrogen The entire target assembly served as a Faraday cup for monitoring the beam

Following the bombardment the target holder was removed from the Hilac and disassembled inside a glove box The gold foil was removed and placed inside a small quartz cup which was heated with an oxygen methane torch The gold foil was melted and the volatile species astatine polonium and certain fission products, were collected on a water-cooled plate usually platinum The activity on this plate served as the source for alpha spectrography recoil collections and α ,′ coincidence measurements As some of the nuclides studied had very short half-lives e g as short as 1 min, the above procedure was carried out as rapidly as possible To expedite moving the sample from the Hilac building to the α-particle spectrograph approximately one-quarter mile the preparation of the source was performed in a glove box mounted on a truck during the trip between buildings The minimum elapsed time recorded between the end of bombardment and start of exposure in the spectrograph was 117 sec

B *α-Particle spectrograph results*

Magnetic analysis was performed with a 180 double-focusing spectrograph(10) employing a photographic plate as the detector With a source 3 mm 20 mm it was possible to obtain an energy resolution of 0 25 per cent at an instrument transmission factor of 5 10^{1} The source was obtained in the form of the indicated

---

(10) R C PILGER, JR , Report UCRL-3877 (1957)

Table 1.—Relative yields for astatine isotopes produced in carbon ion bombardment of gold*

Aluminium absorber thickness (mils)	0	1.25	2	3.25	4.25	6.25	1.25
Gold target thickness (mils)	1	1	1	1	1	1	2
Calculated carbon ion energy	125–92	116–75	108–66	96–51	86–37	59–0	116–0
Isotope relative yields							
1.5 min ^{201}At	0.56	0.28	0.026				0.19
3.0 min ^{202}At { 6.23 MeV	0.17 } 0.46	0.13 } 0.37	0.095 } 0.23	0.03			0.10 } 0.30
3.0 min ^{202}At { 6.13 MeV	0.29	0.24	0.13				0.20
7.4 min ^{203}At	1.0	1.0	1.0	1.0	1.0		1.0
9.3 min ^{204}At		0.23		0.37	1.5		0.17
26 min ^{205}At		0.087		0.54	2.7	1.0	0.36
31 min ^{206}At		<0.0002				0.046	0.0038

* These yields are the relative α-particle intensities at the end of a saturation bombardment.

band by collimation in the volatilization procedure used to separate the astatine fraction from the target.

The energies, half-lives, and relative intensities of the alpha groups of astatine isotopes with mass numbers 200–207 are listed in Table 2. The entry β^+/EC in column 3 of Table 2 means this mode of decay was indicated by the identification of the corresponding polonium daughter collected by a "recoil" process. It should be emphasized that all of the astatine isotopes studied here must be unstable with respect

TABLE 2.—DATA ON ASTATINE ISOTOPES (THIS WORK)

Mass no.	Half-life	Type of decay	α-particle energy (MeV)	Relative intensity (%)
207	1.4 hr	α	5.752 ± 0.008	
206	31.0 ± 1.5 min	α	5.696 ± 0.008	
205	26.2 ± 0.5 min	α	5.896 ± 0.004	
204	9.3 ± 0.2 min	α,β^+/EC	5.948 ± 0.003	
203	7.4 ± 0.3 min	α	6.085 ± 0.001	
202	3.0 ± 0.2 min	α,β^+/EC	6.227 ± 0.003	36 ± 2
	2.9 ± 0.2 min		6.133 ± 0.002	64 ± 2
201	1.5 ± 0.1 min	α,β^+/EC	6.342 ± 0.006	
200	0.9 ± 0.2 min	α,β^+/EC	6.465 ± 0.011	~40
			6.412 ± 0.009	~60

to electron capture and therefore the half-lives listed are not the partial α-decay half-lives.

The α-group of ^{203}At was adopted as an internal energy standard and was first measured relative to ^{242}Cm α-particles in a uniform-field α-particle spectrograph with a more precise energy calibration. This spectrograph, a 60° symmetrical magnetic analyser, has been described elsewhere.[11] A source was prepared on which ^{242}Cm was first deposited through vacuum sublimation followed by the volatilization of astatine 203 from a gold target. The ^{203}At group fell between the two α-groups of ^{242}Cm which lead to the ground state and first excited state of ^{238}Pu. With reference to the energy for the ground state decay of ^{242}Cm (α_0 = 6.110 MeV)[12] and the energy difference between the ground state and first excited state of Pu^{238} (ΔE = 44.11 keV),[13] the value for ^{203}At α-particle energy is 6.085 ± 0.001 MeV. The energies of the other astatine α-groups were measured relative to ^{203}At in the 180° α-spectrograph.

Figures 1a and 1b show the results of successive exposures in the spectrograph through which the half-life associated with each α-group was determined. The isotopic assignments identifying the different decay curves were arrived at through the experiments described in the following section.

C. *Isotopic assignments*

It has already been mentioned that the method for preparing spectrograph sources by melting the gold targets and collecting the volatile species would not yield a pure astatine fraction; in particular, much of the polonium fraction would be expected to

---

[11] F. L. REYNOLDS, *Rev. Sci. Instrum.* **22**, 749 (1951); F. ASARO, F. L. REYNOLDS and I. PERLMAN, *Phys. Rev.* **87**, 277 (1952).

[12] F. ASARO, S. G. THOMPSON and I. PERLMAN, *Phys. Rev.* **92**, 694 (1953).

[13] W. G. SMITH and J. M. HOLLANDER, *Phys. Rev.* **101**, 746 (1956).

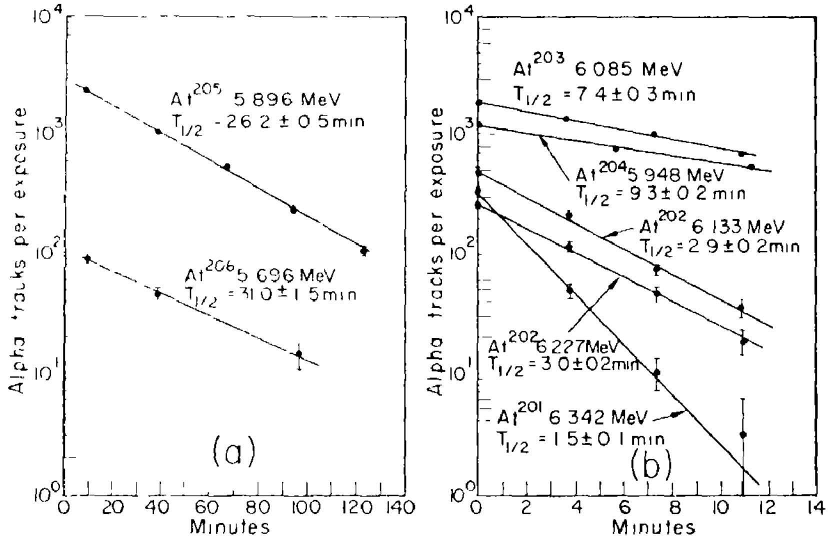


FIG 1 - Decay of $^{201-206}$At α-groups from spectrographic measurements

appear with the astatine The top part of Fig 2 shows a spectrum over a limited range of α-energies from a typical irradiation A second irradiation was then performed under identical conditions after which the platinum plate on which the activities were collected was heated gently over a gas flame before mounting in the spectrograph Although manifestly crude, this form of "blowtorch chemistry" is quite effective in removing astatine without removing appreciable quantities of polonium The bottom part of Fig 2 shows the result of this treatment and, by difference, identifies quite clearly those alpha groups, which belong to astatine A small peak attributed to ^{203}At was present after flaming, but as this comprised less than 1 per cent of the

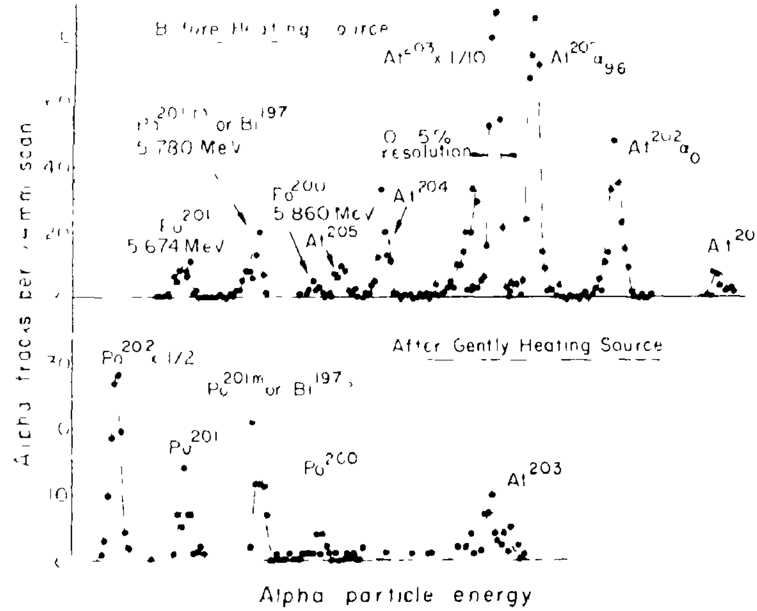


FIG 2 - Astatine-polonium α-spectra before and after gently heating source

amount which should have been present originally, the separation was 99 per cent complete (The energy range covered in the second exposure extended to a slightly lower energy and this accounts for the appearance of the ^{202}Po peak in its spectrum) The astatine α-groups with energies higher than 6 MeV are shown in Fig 3 Two groups are indicated as belonging to ^{202}At because the half-lives were the same (see Fig 1) and because of their constant intensity ratio when different bombardment conditions were employed (see later paragraphs) Similarly, the two weak groups at 6 412 and 6 465 MeV have been assigned to the same isotope, tentatively ^{200}At

The isotopic assignments of the several astatine α-groups were deduced in part from relative yields of the different species upon varying the carbon ion energy The data are summarized in Table 1 The upper section of the table lists the thicknesses of the aluminium energy degrading foils and the carbon-ion energy band expended in each gold target The relative yields of the various alpha emitters pertain to the α-particle intensities *at saturation* In order to obtain these numbers the intensity of each alpha peak was corrected for the decay before counting began and corrected to formation saturation in the bombardment All intensities for each bombardment are normalized to an intensity of unity for the 7 4 min ^{201}At activity except for the experiment in which no ^{203}At α-particles were detected

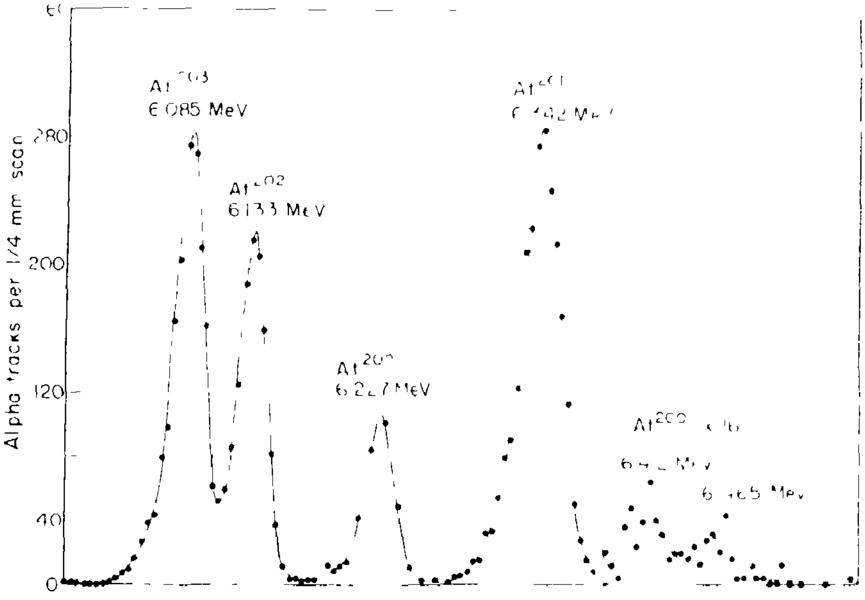


FIG 3 —α-spectra of $^{200-203}$At

Further evidence for the isotopic assignments was found by use of a recoil collection technique It was found that polonium atoms were collected on a plate, either platinum or aluminium, placed 1 cm above a thin volatilized astatine source with a negative potential of 300 V applied to the collector plate A series of collections, usually of equal length, was made The α-activities on the collector plates were followed for decay in an α-pulse-height analyser The activity of each polonium isotope was corrected to the time at the end of each collection to produce a decay curve of the parent (see Fig 4) We postulate the recoil mechanism occurring here involves the electron-capture decay (or less probable positron emission) of the parent astatine nuclei with subsequent collection of positively charged polonium nuclei. If polonium were being lost from the source predominantly by vapourization or ionization caused by collisions with α-particles, one would not expect to see the observed divergence in parent half-lives for the various polonium isotopes.

^{207}At. This well characterized isotope[1,5,6] has been shown in other work to have an alpha particle energy of 5·75 MeV and a half-life of about 1·8 hr. In the present work the ^{207}At serves principally to help identify mass 206. Our best value for the α-particle energy is 5·752 ± 0·008 MeV with a half-life of between 1 and 4 hr.

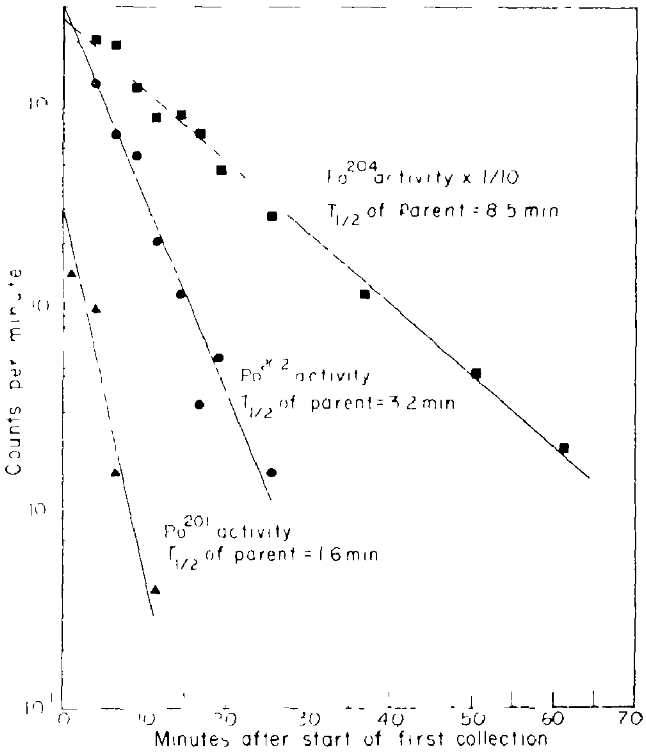


FIG. 4.—Decay curves for ^{201,204,202}At determined from the collection of recoil atoms of polonium.

^{206}At. An isotope of astatine with this mass number was characterized[4,5] as decaying by electron capture with a half-life of about 3 hr. The isotope was prepared by irradiating bismuth with α-particles and identified only through periodic removal of the electron-capture decay product, ^{206}Po. Subsequently, a number of authors have reported ^{206}At to be an α-emitter with a half-life of 20–30 min. In all of these studies heavy ion reactions were used to produce astatine isotopes. The interesting question of whether there are two isomers of ^{206}At will be set aside as we shall only be concerned here with the α-emitter.

Our best values for the half-life and α-particle energy are 31·0 ± 1·5 min and 5·696 ± 0·008 MeV. This half-life, based upon improved statistics, is different from that given in our initial report[3] and is in better agreement with the value 29·5 ± 0·6 min given by LATIMER *et al.*[8] The α-group was formed in measurable yield only with the lowest energy carbon ions and was thus believed to arise from the reaction

^{197}Au(^{12}C, 3n) or possibly ^{197}Au(^{12}C, 2n) There had been rather good evidence that in heavy elements such as gold, C, 2n reactions have very low cross-sections As can be seen from Fig 5, both the 5 696 MeV group and that of ^{207}At were clearly seen in a ^{14}N bombardment of gold In the corresponding carbon ion bombardment (Fig 5) the ^{207}At intensity dropped by nearly two orders of magnitude with respect to the 5 696 MeV group, thus establishing that the latter was not due to an isomer of ^{207}At but probably to ^{206}At Complete excitation functions with carbon and nitrogen ion projectiles using thin targets of gold and separated platinum isotopes gave more convincing proof that this alpha emitter is ^{206}At (9 14)

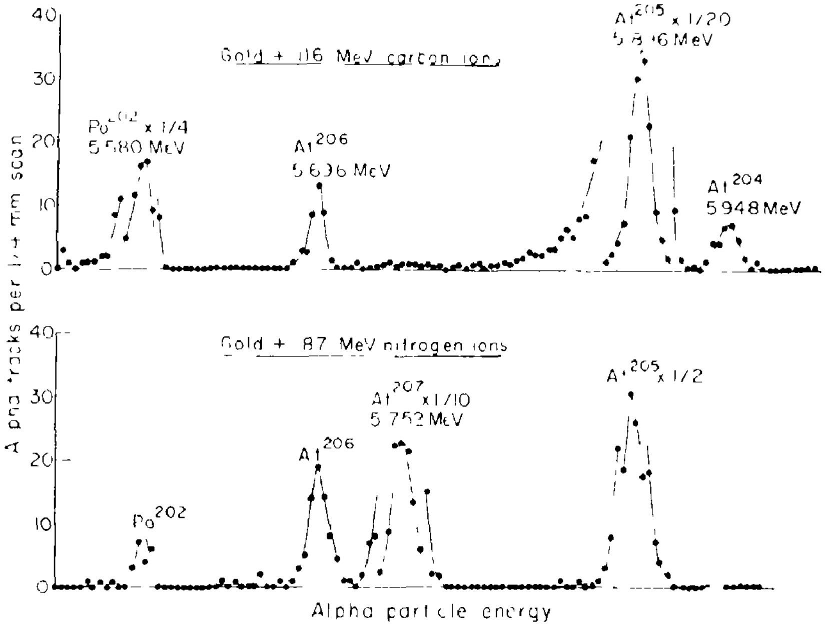


Fig 5 – α-spectra of ^{204} ^{207}At

Latimer *et al* (8) have reported the half-life as 29 5 ± 0 6 min and have found that α-decay is the rare decay mode, as slightly more than 99 per cent of the ^{206}At atoms decay by electron capture Forsling and co-workers(7) apparently obtained some of this activity at mass 206 using a mass separator although there was more than one alpha group present, a finding not in keeping with the present measurements (see later discussion)

^{205}At In the present study, this isotope was presumably made by the ^{12}C, 4n reaction and was the only one detectable other than ^{206}At when the maximum carbon ion energy was 59 MeV Its yield relative to that of At^{206} increased with increase in projectile energy Its half-life was found to be 26 2 ± 0 5 min and the α-energy, 5 896 ± 0 008 MeV This isotope was first identified by Barton *et al* (1) through its genetic relationship with ^{205}Bi A mass separation by Forsling *et al* (7) made the mass assignment definite These authors reported an α-energy of 5 90 ± 0 03 MeV and a half-life of 28 ± 3 min Other workers(9) determined excitation functions for

---

(14) G E Gordon, Report UCRL-9083 (1960)

the Au(C, 4*n*) and Pt(N, 5*n*) reactions, all in agreement with the isotopic assignment ^{205}At

^{204}At The preliminary report on this work$^{(3)}$ gave essentially the same properties as those reported here half-life 9 3 ± 0 2 min α-energy 5 948 ± 0 003 MeV This isotope was the next to appear after ^{205}At when the carbon ion energy was increased to 86 MeV from 59 MeV (see Table 1) It was also possible to collect recoils from its electron capture decay to show that the parent of the ^{204}Po collected had a half-life of about 9 min (see Fig 4) FORSLING *et al* $^{(7)}$ found an isotope of astatine with similar properties at mass 204 although the associated α-group seemed to have an unusual spread for a single group Further confirmation on the mass assignment came from the excitation functions of THOMAS *et al* $^{(9)}$ who found this activity to appear properly for the reactions Au(^{12}C, 7*n*), ^{196}Pt(^{14}N, 6*n*), and ^{198}Pt(^{14}N, 8*n*)

The early work by BARTON *et al* $^{(1)}$, employing the genetic relationship with known bismuth activities obtained evidence of a 25 min period for ^{204}At They could find no α-branching for this isotope of astatine LATIMER, GORDON, and THOMAS$^{(8)}$ could not find this activity when they searched for ^{204}Po in the decay products of an astatine fraction The only difference between the two experiments was that in one case astatine isotopes were made by the irradiation of bismuth with α-particles and in the other with heavy ions on lighter target materials The question of whether or not there are isomers of ^{204}At decaying independently remains unresolved

^{203}At The properties found here for ^{203}At (half-life 7 4 ± 0 3 min, α-energy 6 085 ± 0 001 MeV) are in good agreement with those of BARTON *et al* $^{(1)}$ who gave a tentative mass assignment From Table 1 it can be seen that the appearance of this activity and its relative yield to other activities as the projectile energy was further increased favours the assignment to mass 203 The more complete excitation functions of THOMAS *et al* $^{(9)}$ provide more convincing evidence Finally, FORSLING *et al* $^{(7)}$ showed that a similar isotope appeared at mass 203 when their astatine fraction was mass-separated

^{202}At This isotope has two measurable α-groups, 6 227 ± 0 003 MeV in 36 ± 2 per cent abundance and 6 113 ± 0 002 MeV in 64 ± 2 per cent abundance, and decays with a half-life of 3 0 ± 0 2 min These properties are essentially the same as those given in the preliminary report $^{(3)}$ The data of Table 1 shows that the mass assignment 202 is reasonable The collection of recoils in which ^{202}Po was identified and shown to be the product of a 3 min parent gave further proof The experiments of FORSLING *et al* $^{(7)}$ with a mass separator yielded alpha particles of 6 13 MeV at mass 202 but did not show clearly the second group reported here It is possible that this discrepancy is statistical in origin, since FORSLING *et al* were dealing with very weak samples

It is interesting to note that the activity described here was not seen in the experiments of BARTON *et al* $^{(4)}$, even though they saw clearly the 7 3 min ^{203}At and a 1 7 min activity which will be assigned to ^{201}At This situation resembles the findings already mentioned for the other odd-odd astatine isotope in which different bombardment conditions seem to produce different isomers

^{201}At An α-emitter with a half-life of 1 5 ± 0 1 min and an α-particle energy of 6 342 ± 0 006 MeV has been assigned to ^{201}At It first appeared when the maximum carbon ion energy was 108 MeV and increased in yield relative to ^{202}At as the energy was further increased (see Table 1) The recoil collection technique showed the appearance of ^{201}Po with a half-life for its parent of 1 6 min (see Fig 4) This same activity was seen by BARTON *et al* (4), but they could not establish the mass number other than to say that it was lower than ^{203}At. Similarly, this activity was seen by FORSLING *et al* (7) but in amounts too low to obtain a mass analysis.

^{200}At. Two α-groups with a half-life 0.9 ± 0.2 min and energies of 6.412 ± 0.009 and 6.465 ± 0.011 MeV have been tentatively assigned to ^{200}At. These groups are very likely the same as the 6.50 MeV group seen by BARTON *et al* which had a half-life of 43 sec and was designated as ^{202}At.

Other activities. Several activities not already discussed in detail appeared in these studies. They are evident in Fig. 2, where they are seen to persist when the astatine is removed by gentle heating. Most if not all of these activities have been seen by others, and conclusions as to their identities are summarized in Table 3. Decay curves for these nuclides are shown in Fig. 6.

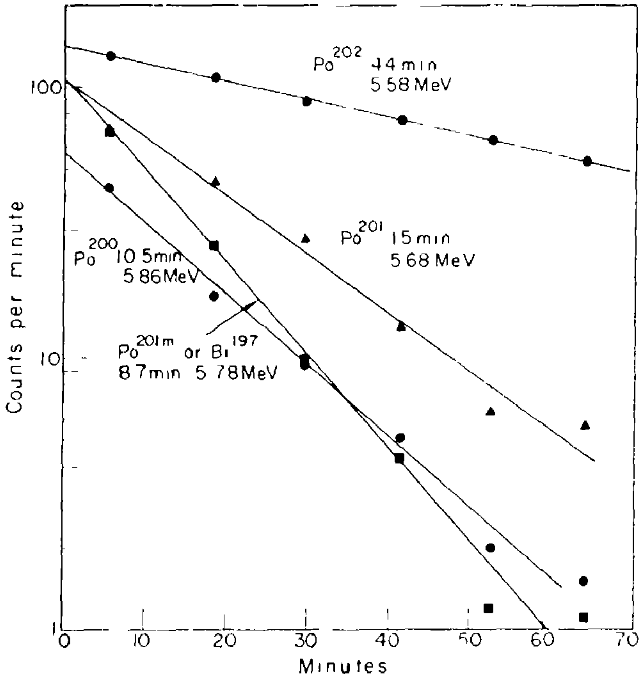


FIG. 6.—Ionization chamber measurement of decay of polonium sample collected as recoil atoms from electron capture of astatine.

^{202}Po. The group at 5.580 ± 0.010 MeV with a half-life of 44 min is identified as ^{202}Po, which has been found to have similar properties by a number of investigators and has been proved by FORSLING and ALVAGER (17) definitely to have the indicated mass number. As already mentioned, the present studies have shown by the recoil collection technique that the ^{202}At parent has a half-life of 3 min. A summary of genetic relations for this and other activities is given in Table 4.

^{201}Po. Similarly, a group at 5.674 ± 0.009 MeV is identified as ^{201}Po, which has been already characterized by others, as summarized in Table 3. Its parent, ^{201}At, has a half-life of 1.5 min.

^{201m}Po(^{197}Bi). An α-group at 5.780 ± 0.007 MeV with a half-life of 8.7 ± 0.6 min is less easy to identify. It is genetically related to an astatine isotope with a half-life of 1.5 min, just as is ^{201}Po. Furthermore, the intensity of the 5.78 MeV group in the

TABLE 3 —POLONIUM α-SPECTRA DATA

Isotope	This work (α-spectrograph data)		KARRAKER *et al* (15)		ROSENBLUM and TYREN (16)		FORSLING and ALVAGER (17)	
	Energy (MeV)	Half-life (min)	Energy (MeV)	Half-life (min)	Energy (MeV)	Half-life (min)	Energy (MeV)	Half-life (min)
^{202}Po	5 580 ± 0 010	44 ± 7	5 59 ± 0 03	52	5 575	~55	5 57 ± 0 03	50 ± 10
^{201}Po	5 674 ± 0 009	19 5 ± 2	5 70	18	5 671	~17	5 57 ± 0 03	<25
							5 67 ± 0 03	
							5 77 ± 0 05	16 ± 3
^{201m}Po or ^{197}Bi	5 780 ± 0 007	8 5 ± 1			5 770*	~8		
^{200}Po	5 860 ± 0 006	9 4 ± 1 6	5 84	11	5 846†	~11	5 75 ± 0 03	
							5 86 ± 0 03	12 ± 4

* From α-systematics, these authors tentatively assigned this group to ^{200}Po

† From α-systematics these authors tentatively assigned this group to ^{199}Po

---

(15) D G KARRAKER, A GHIORSO and D H TEMPLETON *Phys Rev* **83**, 390 (1951), D G KARRAKER and D H TEMPLETON, *Phys Rev* **81**, 510 (1951)

(16) S ROSENBLUM and H TYREN, *C R Acad Sci*, *Paris* **239**, 1205 (1954)

(17) W FORSLING and T ALVAGER, *Arkiv Fysik* **19**, 353 (1961)

TABLE 4 — RECOIL DATA

Isotope	α-particle energy (MeV)	Half-life of Po isotope (min)	Half-life of parent (min)	Parent
^{202}Po	5.58	44.7 ± 2.2	Normalized to 3.0	^{202}At
^{201}Po	5.68	15.3 ± 0.8	1.5 ± 0.1	^{201}At
^{201m}Po or ^{197}Bi	5.78	8.7 ± 0.6	1.5 ± 0.2	^{201}At
^{200}Po ?	5.86	11.0 ± 1.0	0.9 ± 0.1	^{200}At ?

TABLE 5 — RELATIVE YIELDS* OF At ISOTOPES UNDERGOING DECAY TO Po (OR Bi) ISOTOPES

Absorber (Al)	Beam energy (MeV)	Relative yield, for α-particle energy of			
		5.58 MeV (^{202}Po)	5.68 MeV (^{201}Po)	5.78 MeV (^{201m}Po or ^{197}Bi)	5.86 MeV (^{200}Po ?)
None	125-118	1.00	0.24	0.19	0.28
None	125-118	1.00	0.31	0.27	0.17
0.001 in	118-110	1.00	0.12	0.09	0.014

* These yields are the relative At electron-capture decay rates at the end of a saturation bombardment multiplied by the Po α-branching ratios and the recoil efficiencies for the various Po isotopes.

TABLE 6 — RELATIVE YIELDS* OF Po ISOTOPES IN THE α-PARTICLE SPECTROGRAPH EXPERIMENTS

Absorber (Al)	Beam energy (MeV)	Relative yield, for α-particle energy of			
		5.580 MeV (^{202}Po)	5.674 MeV (^{201}Po)	5.780 MeV (^{201m}Po or ^{197}Bi)	5.860 MeV (^{200}Po ?)
None	125-108	1.00	0.29	0.64	0.59
0.001 in	118-97	1.00	0.43	0.76	0.14
0.002 in	108-87	1.00	0.03	0.05	0.02

* These yields are the relative Po alpha decay rates at the end of a saturation bombardment.

recoil spectra follows roughly that of ^{201}Po (5.68 MeV) when the bombardment energy is changed (see Table 5). This also suggests that both alpha groups have the same astatine parent. The data of Table 6 also agree with this interpretation in showing that the 5.674 and 5.780 MeV groups follow each other in intensity in the spectra taken on the astatine fraction without separation from polonium. As both groups with different half-lives have ^{201}At as the parent, this means that either the 5.780 group comes from an isomer of ^{201}Po or from ^{197}Bi (the ^{201}At α-decay product). It is possible that the data of FORSLING and ALVAGER could bear on this question but intercomparisons are sufficiently difficult to discourage any deductions which would result.

^{200}Po. The α-group at 5.86 MeV with a half-life of about 10 min has been assigned by FORSLING and ALVAGER to ^{200}Po. As seen in Tables 4–6, this alpha emitter is only formed at the highest carbon ion energies, and it appears to have a mass number 201. The half-life of its parent agrees well with that associated with the two alpha groups of 6.412 and 6.465 MeV in astatine fraction. As these groups were tentatively assigned to ^{200}At, the 5.860 MeV groups are tentatively assigned to Po^{200}. Our best value for the half-life is 10.5 ± 1 min.

D. *Decay scheme studies*

In an attempt to establish partial decay schemes for the α-decay of the astatine isotopes, a series of α–γ coincidence measurements were performed. The experimental apparatus included a zinc sulphide detector for α-particles and a sodium iodide detector for γ-rays. After condensing the astatine vapours from the target on a 0.001-in. aluminium foil, this source was placed so the α-particles would impinge on the zinc sulphide. The pulse height distribution from the zinc sulphide was such that individual α-groups from the various astatine isotopes could not be resolved. Thus, the α-particle detector was set to feed pulses from a wide range of energies into the coincidence circuit. The actual α-particle pulse-height distribution was measured by counting a separate fraction of the astatine activity in a gridded ionization chamber and pulse-height analyser combination. The γ-radiation from the source penetrated the 0.001-in. aluminium source plate plus a 0.005 in. aluminium reflector to strike the sodium iodide detector, whereas conversion electrons of ~180 keV energy were absorbed by the aluminium. In the α-γ coincidence circuit, the pulses from the two detectors were given appropriate amplification and fed through a coincidence unit with 1.5 μsec resolving time. The γ-spectrum in coincidence with α-particles was recorded with a 100-channel pulse-height analyser.

In Table 7 the results of these measurements are listed in the form of upper limits for photons in the energy range 20–100 keV in coincidence with α-particles from the decay of the isotope listed. Similarly, no coincidences were observed for photons with energy greater than 100 keV. The upper limits for these occurrences necessarily increase with increasing energy due to a decrease in detection efficiency in the sodium iodide crystal for γ-rays above 100 keV.

TABLE 7.—α-γ COINCIDENCE DATA FOR $^{201-206}$At

Isotope	Upper limit for coincident 20–100 keV photons (%)
^{201}At	0.2
^{202}At (6.23 MeV)	0.6
^{202}At (6.13 MeV)	0.5
^{203}At	0.2
^{204}At	1.2
^{205}At	1.1
^{206}At	Observed 68 keV photons in coincidence with 5.70 MeV alphas, in 16 ± 3% abundance

J. Inorg Nucl Chem 1963 Vol 25 pp 117 to 122 Pergamon Press Ltd Printed in Northern Ireland

WATER ASSOCIATED WITH THE BIS(8-QUINOLINOL) DIOXOURANIUM(VI) CHELATE EXTRACTED INTO CHLOROFORM

D R GERE* and C E MELOAN
Department of Chemistry, Kansas State University Manhattan, Kansas

(Received 11 June 1962)

Abstract– The number of molecules of water associated with the 8-quinolinol chelate of uranium (VI) when it was extracted into chloroform was found to be 5 ± 2 molecules

WHEN faced with devising a new extraction separation scheme, one is presented with the problem of deciding what solvent would most advantageously extract the species of interest Very little theory exists in the area of the extraction of metal chelates into immiscible solvents Several empirical rules exist in different areas, but few have general application It is well recognized[1] that the solubilities of the compounds in the respective solvents have little bearing upon the distribution of the species between the two solvents at the liquid junction This may be due to the fact that when comparing relative solubilities of the species between the two solvents, the actual species which is extracted has not been fully identified Perhaps the nature of solvation of the chelates in their respective solvents determines to a large extent where the species will reside when confronted with two differing solvents

MELOAN and BRANDT[2,3] measured the number of water molecules associated with the benzohydroxamic acid chelates of uranium(VI) and iron(III) when extracted into 1-decanol A general relationship was established between the amount of water soluble in a given alcohol and the amount of chelate extracted into that alcohol They found 6 ± 1 molecules of water associated with the uranium(VI) chelate and 9 ± 3 associated with the iron(III) chelate

Although this was the first published account of the measurement of water associated with extracted chelates, SWIFT and AXELROD[4] had been interested in this idea in 1940, relative to the extraction of ferric chloride into ether from aqueous solution This sort of information has been sought more recently in the field of inorganic extractions such as the extraction of hydrated acids described by TUCK and DIAMOND [5]

It was felt that the work on extracted chelates should be extended to see if the association of water molecules was present only in alcohol solvents or only with neutral chelate extractions as opposed to ion-association chelate extractions The purpose of our current research is to determine to what extent if any, the solvent, ligand, anion, and central metal ion play in the associated waters of chelate extractions

---

* Abstracted from a thesis submitted by Dennis R Gere to the graduate school of Kansas State University, May, 1962, in partial fulfillment of the requirements for the degree of Master of Science

[1] G H MORRISON and H FREISER, *Solvent Extraction in Analytical Chemistry* J Wiley, New York (1957)

[2] C E MELOAN Doctoral Thesis, Purdue University (1959)

[3] C E MELOAN and W W BRANDT, *J Inorg Nuc Chem*, **24**, 1645 (1962)

[4] E H SWIFT and J AXELROD, *J Amer Chem Soc* **62**, 33 (1940)

[5] D G TUCK and R M DIAMOND, *J Phys Chem* **65**, 193 1961

Of particular interest is the limit set upon photons in coincidence with the 6.13 MeV group of ^{202}At. Since α-groups at 6.23 MeV and 6.13 MeV are assigned to the decay of 3.0 min ^{202}At, a 100 keV transition or other lower energy multiple transitions might be expected to follow the 6.13 MeV α-group. The upper limit for photons (20–100 keV) of 0.5 per cent in coincidence with the 6.13 MeV α-particles suggests the transition or transitions de-exciting the ^{198}Bi state populated by this α-group are highly converted or delayed. A measurement of the upper limit for *L* X-rays in coincidence with the 6.13 MeV group indicated less than 25 per cent of the 6.13 MeV group is followed by a prompt converted transition, so the transition is apparently delayed. It is possible to postulate alternative schemes involving isomers of ^{202}At with the same half-life which would explain the experimental observations. All such schemes seem less likely explanations than the above suggestion of a delayed transition between two levels in the daughter nucleus.

In the case of ^{206}At, 68 keV photons were observed in coincidence with the 5.70 MeV α-particles in 16 ± 3 per cent abundance. There were no alpha peaks near the 5.70 MeV ^{206}At group with an intensity as high as 16 per cent. Therefore, it is likely the 68 keV γ-ray de-excites the state populated by the 5.70 MeV α-group. The conversion coefficient for this transition, if there are no alternative modes of decay, would be 5.3 ± 1.3. This is in good agreement with the theoretical value of 6.3 for an M1 transition, which was obtained from the theoretical *L*-shell conversion coefficients of Sliv(18) and an empirical value of 0.7 for the ratio of *L*-shell to total conversion. In order to confirm this decay sequence, α-*L* X-ray coincidence measurements were made with the 5.70 MeV group. Because of the relatively large correction due to the absorption of the low-energy *L* X-rays, their intensity is very sensitive to the exact energies. The *L* X-ray intensity corresponds to a conversion coefficient of 9.4 ± 0.9 if all the *L* X-rays originate in the L_{III} subshell, or to a value of 6.0 ± 0.6 if they originate in the L_{I} subshell. These values are roughly consistent with the value of 5.3 ± 1.3 deduced from the γ-ray intensity and confirm the multipolarity assignment. Further confirmation of the decay sequence came from a measurement of the alpha spectrum with a 2π α-chamber coupled to a pulse-height analyser. In this experiment a broad double peak was observed in contrast to the single peak found in the magnetic spectrograph experiment. These observations indicate abundant conversion electrons in coincidence with the 5.70 MeV group.

DISCUSSION

The light astatine and polonium isotopes which we have studied lie just below the major closed shell at 126 neutrons. A plot of alpha decay energy versus neutron number for bismuth, polonium, astatine and radon isotopes (Fig. 7) demonstrates the smooth dependence of decay energy upon neutron number below the closed shell. The light isotopes of both astatine and polonium lie on nearly straight lines in this plot.

Although no experimental evidence is available for the spins and parities of the states involved in the α-decay of the light astatine isotopes, certain information regarding these states can be inferred from experimental measurements of spins of neighbouring nuclides. The spin of the ^{211}At nucleus has been measured and found to be $\frac{9}{2}$ (19) Similarly, the spins of ^{201}Bi, ^{203}Bi, ^{205}Bi, and ^{209}Bi (83rd proton) have been measured and found to be $\frac{9}{2}$ (20, 21) According to shell model theory the 83rd and 85th odd protons are in $h_{9/2}$ states Thus, it might be expected that the alpha decay of the odd-mass isotopes, astatines 201, 203, 205, and 207, involves unhindered transitions between nuclei whose ground states all have $h_{9/2}$ configurations The experimental results for these nuclides are consistent with such a premise since only one α-group was found for each nuclide and there were no photons coincident with these α-groups

---

(18) L. A. Sliv and I. M. Band, *Table of γ-Ray Conversion Co-efficients* Part 2. Physico-Technical Institute, Academy of Science, Leningrad, U.S.S.S. (1958).

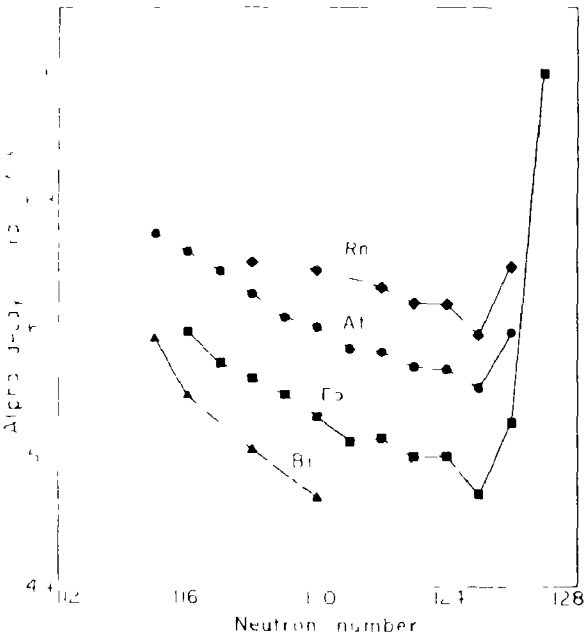


Fig 7 α-decay energy versus neutron number for certain isotopes of Bi Po, At and Rn

In the case of the even-mass astatine isotopes, the coupling of the odd neutron with an $h_{9/2}$ proton must be considered Experimentally measured spins for Po and Bi isotopes with neutron numbers corresponding to astatines 200, 202, 204, 206 and 208 are listed in Table 8

Table 8 Experimentally measured spins for Po and Bi isotopes with neutron numbers corresponding to some even-mass astatine isotopes

Neutron no	Corresponding At isotope	Meas spin of Po isotone(22)	Meas spin of Bi isotone(21)	Configuration in Bi isotone(21)
115	^{200}At			
117	^{202}At	3/2(^{201}Po)	7(^{200}Bi)	$(\pi h_{9/2})(\nu p_{1/2})^{-2}(\nu f_{5/2})^{-6}(\nu p_{3/2})^{-2?}$
119	^{204}At	5/2(^{203}Po)	5(^{202}Bi)	$(\pi h_{9/2})(\nu p_{1/2})^{-2}(\nu f_{5/2})^{-5}$
121	^{206}At	5/2(^{205}Po)	6(^{204}Bi)	$(\pi h_{9/2})(\nu p_{1/2})^{-2}(\nu f_{5/2})^{-3}$
123	^{208}At	5/2(^{207}Po)	6(^{206}Bi)	$(\pi h_{9/2})(\nu p_{1/2})^{-2}(\nu f_{5/2})^{-1}$

---

(19) H L Garvin, T M Green, E Lipworth and W A Nierenberg, *Phys Rev Letters* **1,** 74 (1958)

(20) J E Mack, *Rev Mod Phys* **22,** 64 (1950)

(21) I Lindgren and C M Johansson, *Arkiv Fysik* **15,** 445 (1959), S Axensten, C M Johansson and I Lindgren, *Ibid* 463 (1959)

(22) S Axensten and C M Olsmats, *Arkiv Fysik* **19,** 461 (1961)

The spin values for the polonium isotopes are in agreement with shell model theory. The odd-neutron holes of ^{203}Po, ^{205}Po and ^{207}Po should be in the $f_{5/2}$ level and that of ^{201}Po in the $p_{3/2}$ level.(23) The spin values, both 6, for ^{204}Bi and ^{206}Bi are readily explained by theory,(24) whereas those for ^{200}Bi and ^{202}Bi are not as easily explained on the basis of the extreme single-particle model. Ground state levels in the even-mass astatine isotopes might involve odd neutrons in states other than those considered in the bismuth isotope configurations, e.g., $i_{13/2}$, $h_{9/2}$, or $f_{7/2}$ levels. For an odd neutron in an $i_{13/2}$ level, Nordheim's "strong" rule(25) predicts coupling with an $h_{9/2}$ proton to produce $I = 2-$. Thus, one might encounter M4 isomers in the light even-mass astatine (and bismuth) isotopes with $I = 6-$ and $2-$ or other types of isomers produced by different combinations of spins and parities. Although rather qualitative, these theoretical considerations of the states involved in γ-decay are consistent with the existence of isomerism in the even-mass astatine isotopes (^{206}At?, ^{208}At) and the absence of prompt coincident photons with the 6.13 MeV α-group at ^{202}At.

Acknowledgments.—The authors wish to acknowledge the assistance of Mrs. H. Michel in these experiments. The cooperation of the crew of the Heavy Ion Linear Accelerator in performing the target irradiations is greatly appreciated. Members of the Health Chemistry department were most helpful assisting in the rapid delivery of targets. One of us (R. W. H.) would like to thank Professors G. T. Seaborg and K. Street for their encouragement and cooperation in making his stay at Berkeley possible.

(23) J. Blomqvist and S. Wahlborn, *Arkiv Fysik* **16**, 545 (1959).

(24) S. Wahlborn, *Nucl. Phys.* **3**, 644 (1957).

(25) L. W. Nordheim, *Phys. Rev.* **78**, 294 (1950). K. Way, D. N. Kunder, C. L. McGinnis and R. van Lieshout, *Ann. Rev. Nucl. Sci.* Vol. 6, p. 129. Annual Reviews, Inc., Stanford (1956).

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 1321 to 1342. Pergamon Press Ltd. Printed in Northern Ireland

THICK TARGET RECOIL MEASUREMENTS*

J. A. PANONTIN† and N. SUGARMAN
Enrico Fermi Institute for Nuclear Studies, Department of Chemistry,
University of Chicago, Chicago, Illinois

(*Received* 21 *December* 1962)

Abstract—Corrections for scattering and edge effects affecting thick target recoil results in fission studies are presented. Measurement of the range dispersion of ^{89}Sr and ^{99}Mo from thermal neutron fission of ^{235}U yields 18.2 ± 0.8 and 19.9 ± 0.5 per cent, respectively, for the ratio of the full-width at half maximum of the range distribution in aluminium to the mean range, assuming a Gaussian form for the distribution. Similar determinations for ^{67}Cu, ^{89}Sr and ^{99}Mo from 450 MeV proton fission of uranium give 27.2 ± 6.3, 25.9 ± 1.4, and 23.8 ± 0.6 per cent respectively. The ratio of ranges in the target material, for a thick target, relative to aluminum are presented for fragments from thermal neutron fission of uranium and 450 MeV proton fission of uranium, bismuth, and tantalum. The ranges in aluminium determined by the thick target technique compare favourably with those obtained by the thin target technique.

THE recoil technique has been a valuable method for the study of fission processes(1–5) and other nuclear reactions.(6) Range measurements determine the kinetic energy of a product nuclide. Several factors have been shown to affect the measurements made with either thin or thick targets. A correction for target thickness is required in thin target experiments(1,3) and one for scattering in thick target experiments.(1,2)

This paper reports the results of experiments on the thick target method as used in fission studies. Corrections for the scattering effect based on reported data and for an edge effect found in the present studies are presented. The range dispersion of a given fragment in aluminium has been determined for ^{89}Sr and ^{99}Mo from thermal neutron fission of ^{235}U and for ^{67}Cu, ^{89}Sr and ^{99}Mo from 450 MeV proton fission of ^{238}U. The ratio of ranges of several fission fragments in tantalum, bismuth, and uranium relative to aluminium are also presented. Moreover, the ranges in aluminium determined by the thick target technique are compared with those obtained by the thin target technique.

I. EXPERIMENTAL PROCEDURE

The experimental procedure used is similar to that used in previous high energy recoil studies.(4,5) The target assembly is described in Fig. 1. The target foil is surrounded by a number of thin, ¼ or ½ mil aluminium foils, properly aligned, the number of which is dependent upon the range to be observed. These in turn are separated from similar foils for impurity activation by high purity 1 mil aluminium and the entire assembly is wrapped in 1 mil foil.

---

* This work was supported in part by a grant from the U.S. Atomic Energy Commission.

† Presented in partial fulfillment of the Ph.D. degree in the Department of Chemistry, University of Chicago. The author acknowledges the aid of National Science Foundation fellowship. Now at Argonne National Laboratory, Argonne, Illinois.

(1) J. M. ALEXANDER and M. F. GAZDIK, *Phys. Rev.* **120**, 874 (1960).
(2) J. B. NIDAY, *Phys. Rev.* **121**, 1471 (1961).
(3) F. M. DOUTHETT and D. A. TEMPLETON, *Phys. Rev.* **94**, 128 (1954).
(4) N. SUGARMAN, M. CAMPOS and K. WIELGOZ, *Phys. Rev.* **101**, 388 (1956).
(5) N. T. PORILE and N. SUGARMAN, *Phys. Rev.* **107**, 1410 (1957); **111**, 1747 (1958).
(6) B. G. HARVEY, *Ann. Rev. Nucl. Sci.* **10**, 235 (1960).

The uranium, bismuth and tantalum foils employed were 1 mil, 5 mil, and ½ mil thick, respectively. The isotopic composition of the uranium target was that of the naturally occurring material. The uranium foil surface was chemically cleaned in dilute hydrochloric acid prior to use. Chemical analysis of the bismuth foil indicated greater than 99.99 per cent purity. Within the sensitivity of spectrographic analysis, impurities in the region of the observed fission fragments were found to be absent. The tantalum foil exhibited similar purity.

The thin aluminium foils were of a commercial grade purity. As a result, activation foils were analysed in each experiment and appropriate corrections for impurity activation were made. In the case of the uranium experiments, the corrections were negligible, with the exception of ^{67}Cu for which corrections of the order of 1 to 2 per cent were made, depending upon the activity of the foil. For bismuth and tantalum, the activation corrections ranged from 2 to 10 per cent, depending upon the foil and the nuclide considered.

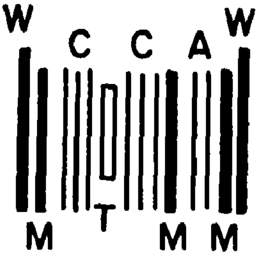


FIG. 1 - Target assembly. *W*, 1 mil aluminium wrapper, *M*, 1 mil aluminium monitor, *C*, ¼ or ⅙ mil aluminium catcher foils, *T*, target, *A*, activation foils (¼ or ⅙ mil).

Foil thicknesses were determined by weighing foils cut to size and measuring areas microscopically. The uranium, bismuth, and tantalum foils were 48.4, 138.8, and 23.3 mg/cm² thick, respectively. The thicknesses were constant to within 1 per cent for uranium and bismuth and to within 2 per cent for tantalum. The ⅙ and ¼ mil aluminium foils had thicknesses of 1.185 and 2.10 mg/cm² respectively, constant to within ½ per cent. Target dimensions were 1.0 cm × 1.5 cm for uranium, 1.5 cm × 0.64 cm for bismuth, and 1.5 cm × 2.0 cm for tantalum. The catcher foils were 1 in. × 1 in. and overlapped the edges of the target foil to ensure the capture of all recoils leaving the target.

The thermal neutron irradiations were performed at the Argonne CP-5 reactor in a flux of 5×10^{11} neutrons cm^{-2} sec^{-1} for a period of one week. The high energy studies used the internal circulating proton beam of the University of Chicago synchrocyclotron at a radius of 76 in., corresponding to a nominal proton energy of 450 MeV. The period of irradiation varied from 1 hr for uranium targets to 2 hours for bismuth and tantalum. Experiments were performed with targets perpendicular, and at 10 degrees, to the beam.

After the irradiations, the target and catcher foils were separated and dissolved for radiochemical analysis. With the exception of the experiments in which tellurium and ruthenium were isolated, the uranium targets were dissolved in 6N HNO_3 in the presence of HCl. For those experiments where ruthenium or tellurium was isolated, the solution procedures of reference (2) were used, for both the target and the catcher foils. The bismuth foils were dissolved in concentrated HNO_3. Hydrofluoric acid in the presence of concentrated nitric acid was used to dissolve the tantalum targets. The aluminium catcher foils were dissolved in a mixture of 6N HCl and HNO_3. The target solutions with the exception of those of tantalum were diluted to 500 ml while the catcher solutions were diluted to 25 ml. Duplicate samples of the catcher foil and quadruplicate samples in the case of the uranium and bismuth target solutions agreed to within 1-2 per cent. Due to the low activity resulting from tantalum targets, entire catcher and target foils were analysed.

Copper

Copper carrier (~15 mg) was added as $Cu(NO_3)_2$ to 5 ml aliquots(5). Copper was precipitated as CuI, dissolved in 6M HNO_3, and a $Fe(OH)_3$ scavenge performed with NH_4OH. A AgI precipitation followed and copper was reprecipitated as the iodide and then as the hydroxide with NaOH. Following the solution of the hydroxide precipitate in 6M HNO_3, the cycle was repeated several times. The copper was finally precipitated as CuI.

Strontium

Strontium carrier (~20 mg) was added as $Sr(NO_3)_2$ to 5 ml aliquots.[2] Strontium was precipitated twice as the nitrate with fuming nitric acid in the presence of sodium and fluoride hold-back carriers. A ferric hydroxide scavenge was then performed, followed by a barium chromate precipitation from a slightly acidic solution containing acetic acid ammonium acetate buffer. The scavenge procedures were repeated and strontium carbonate precipitated.

Molybdenum

Molybdenum carrier (~15 mg) was added as $(NH_4)_6Mo_7O_{24}$ to 5 ml aliquots. Two procedures were used and in the case of the tantalum experiments, both procedures were employed in succession to eliminate excessive activity of ^{24}Na in the aluminium catchers.

Molybdenum was precipitated with α-benzoin oxime[7] in the presence of oxalic acid and the precipitate dissolved in a $HClO_4$-HNO_3 acid mixture. Two $Fe(OH)_3$ scavenges were performed and the cycle repeated several times. The molybdenum was precipitated for mounting as the 8-hydroxyquinolate.

Molybdenum and ferric carrier[8] were extracted from a 6N HCl solution, containing tellurium as a hold-back carrier, with ether equilibrated with acid of the same molarity. $NaBrO_3$ was added before the extraction to ensure complete oxidation of the molybdenum to the 6 oxidation state. After back-extracting the molybdenum and iron, two $Fe(OH)_3$ scavenges were performed. The molybdenum was then precipitated with 8 hydroxyquinoline.

Ruthenium

Ruthenium carrier (~30 mg) was added as $RuCl_3$ to 5 ml aliquots.[2] The solution was treated with KIO_4 in alkaline solution, followed by NaOCl. After standing, $Na_2S_2O_4$ was added and the precipitate dissolved in 6N HCl containing a few drops of concentrated HNO_3. Upon dilution concentrated H_2SO_4 was added and the ruthenium distilled from a $NaBiO_3$-H_2SO_4 solution into 12 N NaOH. The ruthenium was precipitated with ethyl alcohol, dissolved in concentrated HCl and finally precipitated as the metal with magnesium. The total ruthenium activity was counted initially. The ^{106}Ru was counted separately through 40 mg/cm^2 of aluminium to absorb the weak β-rays from ^{103}Ru. The ^{103}Ru activity in the total was estimated by correcting for the ^{106}Ru activity from its absorption characteristics.

Cadmium

Cadmium carrier (~12 mg) was added as $Cd(NO_3)_2$ to 5 ml aliquots.[9] CdS was precipitated in slightly acidic solution (orange to methyl red indicator) and dissolved in 6N HCl. A PdS scavenge was followed by two $Fe(OH)_3$ precipitations in a buffered ammoniacal solution. The cycle was repeated several times and the cadmium was precipitated for counting as cadmium anthralate. The total cadmium activity of ^{115}Cd and ^{115m}Cd was counted initially and after an appropriate time the ^{115m}Cd, separately. The ^{115}Cd activity was obtained by extrapolating the ^{115m}Cd activity to the time of the initial measurements and subtracting its contribution.

Tellurium

Tellurium carrier (~45 mg) in a HNO_3-HCl mixture was added to 5 ml aliquots and evaporated to dryness.[2] The residue was dissolved in 4N HCl heated and tellurium precipitated as the metal with $SnCl_2$. The tellurium was dissolved in a few drops of concentrated HNO_3 and evaporated to dryness. The residue was dissolved in 2N HCl, heated and a $Fe(OH)_3$ scavenge performed. The solution was acidified to 4N HCl and tellurium precipitated with SO_2. The ferric hydroxide and SO_2 precipitations were repeated several times. The tellurium was precipitated as the metal with SO_2 for mounting.

---

(7) J. Kleinberg (Editor) Report LA-1721 Collected Radiochemical Procedures p. 121, U.S.A.E.C. (1954).

(8) D. R. Wills Thesis, M.I.T. (1953).

(9) J. Kleinberg (Editor) Report LA-1721 Collected Radiochemical Procedures p. 142 U.S.A.E.C. (1954).

The final precipitates were filtered onto circular paper disks over a 2.86 cm² area, dried, weighed, mounted on $\frac{1}{16}$ in. aluminium cards and covered with cellophane. Activity measurements were made with several end-window methane-flow proportional counters operating at 4000 V. Due to the large number of samples involved for each nuclide, the decay of one target sample was followed as a standard. The activities of the remaining samples were then determined relative to this standard. Errors from unlike counter characteristics were eliminated by rotating the samples among the remaining counters. This counting procedure was followed over several half-lives for each nuclide investigated. Before counting measurements were made, all counters were checked and adjusted if necessary to maintain the reading of a standard U_3O_8 source within ½ per cent. Empirical self-absorption corrections were applied to the various samples which were adjusted to a constant weight for comparison. The weights of precipitates varied from experiment to experiment within the following limits: ^{67}Cu, 36 ± 2 mg, ^{91}Sr, 31 ± 1 mg, ^{99}Mo, 41 ± 2 mg, ^{103,106}Ru, 21 ± 2 mg, ^{115,115m}Cd, 40 ± 2 mg, and ^{129m,132}Te, 40 ± 2 mg.

II. RESULTS

1. *Thick target corrections*

A. *Scattering effect.* Ranges in aluminium for various fragments from the thermal neutron fission of 1 mil uranium foil were determined by differential experiments using approximately 2.1 mg/cm² aluminium for the first catcher foil. The range was determined from the relation

$$\frac{F(>t)}{F(>0)} = \left(1 - \frac{t}{R_{Al}}\right)^2 \tag{1}$$

where $F(>t)$ is the fraction of the total activity beyond a thickness t mg/cm² of aluminium, $F(>0)$ is the fraction of the total activity escaping from one surface of the target, and R_{Al} is the range in aluminium in mg/cm². A correction for the edge effect described in (Sec. II, 1 B) was applied by multiplying the experimental values of $F(>0)$ by 0.9957. The results are presented in Table 1. The values of R_{Al} (column 4) for ^{89}Sr and ^{115}Cd were found to be 5 and 2 per cent lower, respectively, than corresponding values obtained by the thin target technique (column 7). Range values reported by ALEXANDER and GAZDIK are used for comparison since experimental uncertainties or differences in thickness measurements of aluminium catchers between the two experiments have been minimized. Several foil thicknesses measured independently agreed to within 0.2 per cent.

In the 450 MeV proton fission of 5 mil bismuth foil, ranges in aluminium were determined by use of different thicknesses of aluminium catchers from the relations:(1)

$$\frac{F_{(F,B)}(>t)}{F_{(F,B)}(>0)} = \left(1 - \frac{t}{R_{Al(F,B)}}\right)^2 \tag{2}$$

$$R_{Al} = \frac{R_{Al(F)} + R_{Al(B)}}{2} \tag{3}$$

where the subscripts F and B refer to the forward and backward directions with respect to the proton beam. The ranges so determined differ by less than 1 per cent from those obtained from expressions correcting for the velocity of the struck nuclei and for the anisotropy of the fission process. The results are presented in Table
The values of R_{Al} (column 7) for a given fission product were found to vary wi thickness of catcher foil, t, after correction for the target edge effect.

A scattering correction was made based on reported data(2) and data obtained

TABLE 1.—RANGES OF FISSION FRAGMENTS IN ALUMINIUM FROM THERMAL NEUTRON FISSION OF THICK AND THIN URANIUM TARGETS

Nuclide	Thick target					Thin target[1]
	t (mg/cm² Al)	$\frac{F(\geq t)^*}{F(\geq 0)}$	R_{Al} (uncorr.) (mg/cm²)	$\frac{F(\geq t)\dagger}{F(\geq 0)}$	R_{Al} (corr.) (mg/cm²)	
^{89}Sr	2.114	0.2143	3.94 ± 0.02‡	0.2246	4.02 ± 0.02‡	
	± 0.008	± 0.0014		± 0.0015		
		0.2166	3.95	0.2270	4.04	
	2.108	0.2188	3.96	0.2294	4.05	
		0.2162	3.94	0.2266	4.02	
	2.104	0.2152	3.92	0.2256	4.01	
		0.2168	3.94	0.2273	4.02	
		Average	3.94 ± 0.004**		4.03 ± 0.008**	4.12 ± 0.02
^{99}Mo	2.087	0.2060	3.82 ± 0.02‡	0.2152	3.89 ± 0.02‡	
	± 0.008	± 0.0013		± 0.0014		
		0.2041	3.81	0.2132	3.88	
	2.085	0.2003	3.77	0.2094	3.84	
		0.2042	3.80	0.2134	3.87	
	2.088	0.2030	3.80	0.2121	3.87	
		0.1992	3.77	0.2081	3.84	
	2.114	0.1940	3.78	0.2027	3.85	
		0.2014	3.84	0.2104	3.91	
	2.108	0.1938	3.77	0.2025	3.83	
		0.1972	3.79	0.2061	3.86	
	2.104	0.1959	3.77	0.2047	3.84	
		0.2015	3.81	0.2105	3.89	
		Average	3.79 ± 0.007**		3.86 ± 0.007**	
^{115}Cd	2.087	0.1309	3.27 ± 0.01‡	0.1361	3.31 ± 0.01‡	
	± 0.008	± 0.0009		± 0.0009		
		0.1249	3.23	0.1298	3.26	
	2.085	0.1269	3.24	0.1319	3.27	
		0.1290	3.25	0.1341	3.29	
	2.088	0.1315	3.28	0.1367	3.31	
		0.1280	3.25	0.1331	3.29	
		Average	3.25 ± 0.008**		3.29 ± 0.008**	3.33 ± 0.04

* The value of $F(\geq 0)$ has been decreased by the factor 0.9957 for the edge effect.

† The value of $F(\geq 0)$ has been decreased by the scattering correction factors 0.954, 0.957, and 0.962 for ^{89}Sr, ^{99}Mo, and ^{115}Cd respectively (Fig. 2).

‡ Estimate of cumulative error.

** Standard deviation from the mean.

this laboratory. Differences in the scattering properties of uranium and lead were considered negligible. Ranges in uranium of fission products determined with lead catchers were considered to be unaffected by scattering. The ratio of the range in uranium for a given fission product determined with lead catchers to the range as determined with aluminium catchers was plotted vs. mass number (Fig. 2). It was assumed that the scattered recoils add only to the activity of the foils adjacent to the target since the thickness of these foils was at least 25 per cent of the range. For a given fission fragment, $F(\geq 0)$ was then multiplied by a scattering correction factor from Fig. 2 and a corrected range in aluminium calculated. The correction factors for

TABLE 2.—RANGES IN ALUMINIUM* FOR FISSION PRODUCTS FROM 450 MeV PROTON FISSION OF BISMUTH

Nuclide	t (mg/cm² Al)	$\frac{F_F(>t)}{F_F(>0)}$†	R_{Al_F} (mg/cm²)	$\frac{F_B(>t)}{F_B(>0)}$†	R_{Al_B} (mg/cm²)	R_{Al} (uncorr.) (mg/cm²)	$\frac{I_F(>t)}{I_F(>0)}$‡	R_{Al_F} (mg/cm²)	$\frac{I_B(>t)}{I_B(>0)}$	R_{Al_B} (mg/cm²)	R_{Al} (corr.) (mg/cm²)
^{67}Cu	1.185	0.4964	4.01	0.4414	3.53	3.77	0.5242	4.29	0.4661	3.73	4.01
	±0.008**	±0.0034	±0.04	±0.0026	±0.03	±0.05	±0.0036	±0.04	±0.0027	±0.03	±0.05
	2.110	0.2457	4.16	0.1868	3.70	3.93	0.2595	4.28	0.1973	3.78	4.03
	±0.008	±0.0016	±0.02	±0.0013	±0.02	±0.02	±0.0017	±0.02	±0.0013	±0.02	±0.03
	2.116	0.2420	4.17	0.1814	3.69	3.93	0.2556	4.28	0.1916	3.76	4.02
	2.118	0.2421	4.17	0.1783	3.67	3.92	0.2557	4.28	0.1883	3.74	4.01
	2.270	0.2111	4.20	0.1544	3.74	3.97	0.2229	4.30	0.1630	3.81	4.05
^{99}Mo	1.185	0.3954	3.19	0.3256	2.76	2.98	0.4132	3.32	0.3402	2.84	3.08
	±0.008	±0.0022	±0.02	±0.0018	±0.01	±0.02	±0.0023	±0.02	±0.0019	±0.01	±0.02
	1.185	0.3958	3.19	0.3271	2.77	2.98	0.4136	3.32	0.3418	2.85	3.09
	2.100	0.1253	3.25	0.0687	2.85	3.05	0.1309	3.29	0.0718	2.87	3.08
	±0.008	±0.0008	±0.01	±0.0005	±0.01	±0.01	±0.0009	±0.01	±0.0005	±0.01	±0.01
	2.104(F) 2.088(B)	0.1232	3.24	0.0715	2.85	3.05	0.1287	3.28	0.0747	2.87	3.08
^{115}Cd	1.185	0.3653	3.00	0.3070	2.66	2.83	0.3797	3.09	0.3191	2.72	2.91
	±0.008	±0.0022	±0.02	±0.0019	±0.02	±0.03	±0.0023	±0.02	±0.0019	±0.02	±0.03
	1.185	0.3618	2.97	0.3044	2.64	2.81	0.3761	3.06	0.3164	2.71	2.89
	2.100	0.0985	3.06	0.0525	2.72	2.89	0.1024	3.09	0.0546	2.74	2.92
	±0.008	±0.0007	±0.01	±0.0003	±0.01	±0.01	±0.0007	±0.01	±0.0004	±0.01	±0.01
	2.104(F) 2.088(B)	0.0961	3.05	0.0556	2.73	2.89	0.0999	3.08	0.0578	2.75	2.92

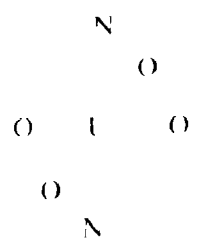
* To within 1 per cent the quoted ranges are equal to ranges determined by more specific equations which include corrections for the velocity of the struck nucleus and the anisotropy of the fission process.

† $F_F(>0)$ and $F_B(>0)$ have been decreased by the factor 0.9678 for the edge correction (Sec. II B).

‡ $F_F(>0)$ and $F_B(>0)$ have been decreased by the scattering correction factors 0.947, 0.957 and 0.962 for ^{67}Cu, ^{99}Mo and ^{115}Cd, respectively.

** The individual errors quoted are estimates of the cumulative experimental error.

The first phase of this investigation which is reported here concerned the extraction of bis(8-quinolinol)dioxouranium(VI) from aqueous solution into chloroform a solvent with different properties compared to 1-decanol the solvent used previously by Meloan and Brandt. This particular chelate is considered to be similar to the benzohydroxamic acid chelate in that 8-quinolinol loses a proton when reacted with the dioxouranium(VI) *ion* such as $UO_2^{2+} + 2C_9H_7ON \rightarrow UO_2(C_9H_6ON)_2 + 2H^+$. The structure of such a chelate would be



APPARATUS

Beckman Model DB Spectrophotometer. All spectrophotometric data were obtained using a Model DB recording spectrophotometer equipped with matched 1.00 cm silica cells.

KF-3 *Aquameter.* A Beckman KF-3 aquameter was used for the automatic titration of the water using the dead stop endpoint detection system. The KF-3 permitted the method to be free of human error inherent in colour judging, eliminated distinguishing between true and false endpoints, and permitted the titration of coloured solutions.

pH measurements. All pH measurements were made using either a Beckman Zeromatic or a Beckman Model H pH meter.

REAGENTS

The dry methanol, the standard water solution, pyridinium iodide, and the Karl Fischer *reagent were prepared as described by* Meloan *and* Brandt.[4]

0.0100M *Dioxouranium(VI).* Dioxouranium(VI) nitrate dihydrate was prepared from the nominally hexahydrate by desiccation over concentrated sulfuric acid for several days. *The number of waters of hydration was then checked by titration of weighed amounts of the solid with* Karl Fischer *reagent.* The aqueous solution was then prepared by weight.

Chloroform. Reagent grade chloroform was distilled before using.

Water. Ion-free water was prepared by running distilled water through a column of mixed bed ion exchange resins previously treated to insure water with a specific resistance of greater than 10^6 Ω/cm, as described by Samuelson.[6]

8-*Quinolinol.* Reagent grade dissolved in chloroform.

METHOD

The method used throughout the entire investigation was essentially that of Meloan and Brandt[4] with suitable variations when necessary. The Karl Fischer reagent technique as described by Meyers *et al.*[7] was used to measure the amount of water present in the organic solvents.

The amount of water in the organic solvent was determined with the aqueous phase containing all components except the chelate itself. This comprised the blank determination. Solutions were then made up containing varying concentrations of the chelate in the organic phase. The amount of water was determined in the organic phase of each of the concentrations. The number of moles of water present in a given volume of organic phase was plotted against the number of moles of chelate present in the same given volume of organic phase. The concentration of chelate present was determined spectrophotometrically.

---

[6] O. Samuelson, *Ion Exchangers in Analytical Chemistry*, p. 259, (3rd printing) J. Wiley, New York (1956).

[7] R. J. Meyers, D. E. Metzler and E. N. Swift, *J. Amer. Chem. Soc.* **72**, 3767 (1950).

scattering of Fig 2 were used for uranium, bismuth and tantalum targets since range-straggling parameters for all of these targets are expected to be approximately the same for a given fission product

The effect of the scattering correction on R_{U1} of fragments from thermal neutron fission of uranium is shown in column 6 of Table 1, and is found to decrease the deviation of the differential range measurements in aluminium with thick and thin targets to 1 2 per cent The significance of this variation, if real, is discussed in Sec II 4 In the bismuth experiments, the scattering correction removed the apparent variation of the range as determined with different thicknesses of catcher foils (Table 2 column 12)

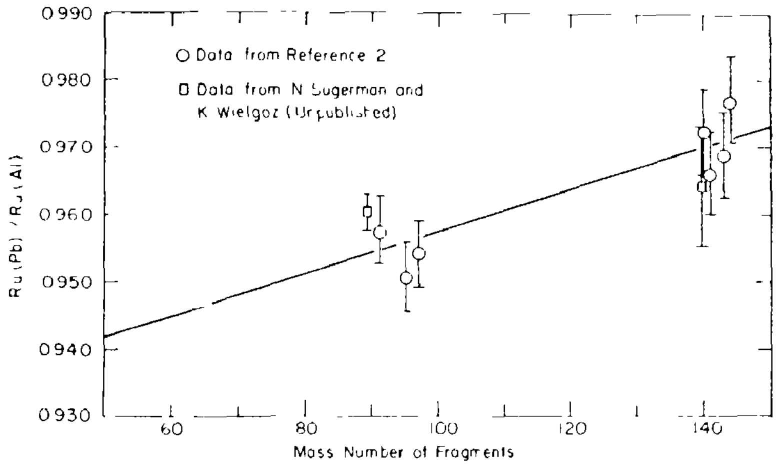


FIG. 2 Ratio of ranges in uranium measured with lead and aluminium catchers vs mass number of fragment ○ Data from Reference (2) □ Data from N SUGARMAN and K WIELGOZ (unpublished)

The scattering corrections used are based on the assumption that the uranium ranges measured with lead catchers are correct and the differences between corresponding ranges as determined with aluminium catchers can be ascribed to scattering at the interface It is expected, however that there should be a small scattering correction even in the case of the lead catcher experiments The integral recoil equations for a thick target have been determined taking into consideration isotropic scattering at the end of the range for a catcher having similar scattering properties as the target A fractional correction given by $1/3\,(R_S/R_1)^2$ where R_S is the radius of the scattering sphere and R_1 is the range in the target or catcher material was calculated For uranium, R_S/R_1 is approximately 0 06 where R_S is calculated from the critical velocity at which scattering occurs and Bohr's range-energy formulation [6, 10] The correction expected is a 0 1 per cent decrease of the range in uranium as determined with lead catchers A similar effect exists at the interface of two catchers foils when isotropic scattering occurs Values of R_S/R_1 calculated from the data of PETRZHAK *et al* [11] for light gases is approximately 0 09 giving rise to a 0 0027 decrease in the

---

[10] N BOHR, *Kgl Danske Vidensk Selsk Mat-fys Medd* **18**, No 8 (1948)

[11] K A PETRZHAK, YU G PETROV and I A SHLYAMIN *J Exp Theor Phys USSR* **38**, 1723 (1960) Translation *Soviet Physics JETP* **11**, No 6 1244 (1960)

value of $F(-t)/F(-0)$, or a decrease in R_{Al} (corr.) of about 0.5 per cent for the uranium data and 0.5 to 1 per cent in the bismuth case. The correction for ranges in uranium is insignificant and the correction for ranges in aluminium has been disregarded in view of the uncertainty in applying this scattering model to fission fragments stopping in aluminium.

B. *Edge effect.* During the course of this investigation, ranges in uranium from 1 mil targets bombarded with 450 MeV protons were found to be on the average 2 per cent lower than values obtained from 3 mil targets (Table 3 Columns 4 and 8) as determined by the equation

$$R_{\mathrm{U}} = \frac{2W\,[F_{\mathrm{F}}(-0) + F_{\mathrm{B}}(-0)]}{1 + \eta^2} \tag{4}$$

where η^2 is a small correction (~0.1 per cent) resulting from the velocity of the struck nucleus, R_{U} is the range in uranium in mg/cm², and W is the target thickness in mg/cm². On the other hand, the range of ^{90}Sr in aluminium for 1 mil uranium was found to be 1 per cent higher than for 3 mil uranium. The discrepancies in range suggested an edge effect, in which fragments recoiling from the surface of the target edges increased the apparent range in the target material and decreased the range in the absorber, by increasing the activity of the foils adjacent to the target.

Recoils emanating from the edges of a target are neglected in the equations for analysing recoil data from thick targets. A correction for these recoils is therefore required. The number of recoils escaping from a surface is proportional to its area and the beam intensity of the particles bombarding the surface.

For the case of the thermal neutron fission of uranium, the neutron intensity may be considered uniform over the target surface area. The number of recoils emanating from surfaces A, Re A (see Fig. 3), which is the number to be considered for range calculations, is related to the *total* recoils observed in the catcher foils, Re T, by the following expression

$$\mathrm{Re}\,A = \beta\,\mathrm{Re}\,T \tag{5}$$

where

$$\beta = \frac{ab}{ab + (a + b)t}$$

and a, b, t, are the target dimensions, t representing the thickness.

In the proton bombardments, the beam intensity varies radially across the target. The average intensity is αI_0, where I_0 is the intensity at the leading edge of the target. The radial dependence of the beam intensity can be expressed by an exponential with a half-value of $T_{\frac{1}{2}}$ cm. This value is determined experimentally by measuring the ^{24}Na activity of ¼-in. squares cut from a one square inch aluminium monitor, and α is calculated from

$$\alpha = \frac{\int_0^{T'} \exp(-0.693T/T_{\frac{1}{2}})\,dT}{\int_0^{T'} dT} \tag{6}$$

where T' is the effective radial length over which the beam intensity is to be average

TABLE 3.—RANGES IN URANIUM DETERMINED WITH 1- AND 3-MIL TARGETS (UNCORRECTED FOR SCATTERING)

	1 mil				3-mil			
Nuclide	W (mg/cm² U)	$F_F(>0) - F_B(>0)$	R_T (mg/cm²) (uncorr.)	R_T* (mg/cm²) (corr.)	W (mg/cm² U)	$F_F(>0) - F_B(>0)$	R_T (mg/cm²) (uncorr.)	R_T* (mg/cm²) (corr.)
⁶⁷Cu	48.43	0.1302	12.58					
	±0.24	±0.0005	±0.08					
	48.43	0.1306	12.63					
	48.02	0.1319	12.65					
		Average	12.62	12.56		Average	12.82†	12.54†
			±0.02	±0.02			±0.06	±0.06
⁸⁹Sr					146.0	0.03859	11.26	
					0.7	±0.00014	±0.07	
					146.0	0.03885	11.33	
	48.43	0.1131	10.94	10.89		Average	11.30	11.05
	0.24	±0.0004	±0.07	0.07			±0.04	±0.04
						Average	11.29†	11.04†
							±0.07	0.07
⁹⁹Mo	48.50	0.1046	10.13					
	±0.24	±0.0004	±0.06					
	48.50	0.1053	10.20					
	48.43	0.1052	10.18					
	48.43	0.1069	10.33					
		Average	10.21	10.16				
			0.05	0.05				
¹⁰⁹Cd	48.50	0.09976	9.67					
	±0.24	0.00035	0.06					
	48.50	0.09858	9.55					
	48.43	0.09897	9.59					
	48.43	0.09892	9.57					
		Average	9.60	9.55		Average	9.81†	9.60†
			0.03	±0.03			±0.04	±0.04
¹¹⁵ᵐCd	48.50	0.09498	9.19					
	0.24	0.00033	0.06					
	48.50	0.09460	9.16					
	48.43	0.09487	9.18					
	48.43	0.09565	9.24					
		Average	9.19	9.15		Average	9.44†	9.24†
			0.02	0.02			±0.03	±0.03

---

* The ranges quoted here are corrected only for the edge effect. No correction for scattering or for the anisotropy of the fission fragment distribution has been made. The edge effect correction factors from Table 4 are 0.9951 and 0.9783 for 1-mil and 3-mil targets, respectively.

† The ranges are those determined by SUGARMAN and co-workers, University of Chicago, unpublished work.

In this case, the corrected number of recoils in terms of the total number is given by

$$\mathrm{Rc}\,A' = \beta'\,\mathrm{Rc}\,T \tag{7}$$

where

$$\beta' = \frac{hT}{hT + \left(T + \dfrac{h}{2\gamma}\right)t}$$

Expressing the recoils as a fraction of the total fragments produced, the corrected fraction, $F_{\mathrm{corr}}(\;0)$, is then given by

$$F_{\mathrm{corr}}(\;0) = (\beta \text{ or } \beta')F_{\mathrm{obs}}(\;0)$$

where $F_{\mathrm{obs}}(\;0)$ is the fraction measured Values of β and β' are given in Table 4 for the various targets employed as well as for the target position with respect to the beam Correction of the ranges from 1 mil and 3 mil targets for this effect leads to good agreement of the values (Table 3, Columns 5 and 9)

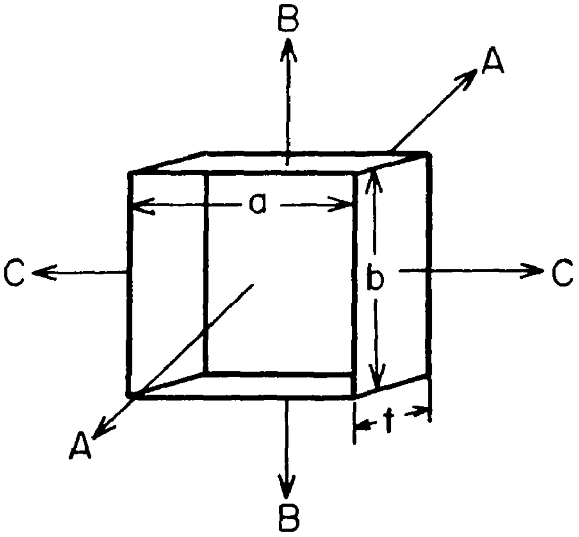


FIG 3 — Diagram of target surfaces showing surfaces B and C responsible for edge effect

2 *Range distributions in aluminium*

When sufficiently thin foils are employed in the differential technique, recoil activity can be observed in foils beyond the average range Excluding such factors as non-uniformity of the foils, thermal diffusion of the fragments, Rutherford scattering of the initially charged fragments, and non-uniformity in the target surface the effects of which were considered and found to be negligible, the observed dispersion can be attributed to scattering near the end of the range from atomic and nuclei collisions and to an energy dispersion in the fission process [12]

Range straggling of particles arising from nuclear and atomic collisions has been

---

[12] F Suzor, *Ann Phys* **4**, 269 (1949)

TABLE 4.—CORRECTION FACTORS FOR EDGE EFFECT

Target and bombarding particle	*t* cm (10^3)	*b* (cm)	*a* or *T* (cm)	Γ_1(cm) Parallel	Γ_1(cm) Perp	α (cm) Parallel	α (cm) Perp	β or β Parallel	β or β Perp
1 mil U thermal neutrons	2.59	1.50	1.00					0.9957	
1 mil U 450 MeV protons	2.59	1.50	1.00	0.334	0.318	0.422	0.407	0.9952	0.9951
3 mil U 450 MeV proton	7.71	1.50	0.635		0.169		0.356		0.9783
5 mil Bi 450 MeV protons	14.05	1.50	0.639	0.291	0.243	0.514	0.460	0.9702	0.9678
½ mil Ta 450 MeV protons	1.40	2.00	1.27	0.303	0.287	0.325	0.311	0.9976	0.9976

Parallel and perpendicular refer to the target position with respect to the beam considered by BOHR(10) and found to be expressible by a Gaussian distribution of the form (12)

$$P(R)\,dR = \frac{1}{\sqrt{(2\pi)}\,\rho R_0}\exp\left(-(R-R_0)^2/2\rho^2 R_0^2\right)dR \tag{8}$$

where R and R_0 refer to the range of the fragment, R_0 being the average range. The straggling parameter ρ is modified from that given for the nuclear stopping region(13) and can be expressed by

$$\rho^2 = \frac{2}{3}\left(\frac{R_N}{R_0}\right)^2\frac{M_1 M_2}{(M_1+M_2)^2} \tag{9}$$

where R_N refers to the average range in the nuclear stopping region and M_1 and M_2 are the masses of the moving and stopping atoms respectively. BOHR's value(10) of ρ^2 is greater by a factor of two.

The kinetic energy distribution from fission of a given fragment has been studied by several investigators(14–17). The range dispersion of a number of fragments in various materials for several fissionable nuclei have also been determined(11, 18, 20). From an analysis of the range straggling of ^{87}Br and ^{137}I from the thermal neutron fission of ^{235}U in various light gases and the assumption of a linear range-velocity dependence, GOOD and WOLLAN calculated the ratio of the full-width at half-maximum to the mean energy for the energy distributions of the light and heavy fragments of about 8 and 5 per cent respectively.(18) The value for ^{87}Br is to be compared with the value 10.8 ± 1.2 per cent, reported by STEIN(16) for mass number 97, determined by time of flight technique. PETRZHAK *et al.*,(11) from range dispersion measurements in various gases, performed in a manner similar to that of GOOD and WOLLAN,(18 report the ratio of the full-width at half-maximum to the mean energy for the energy distributions from fission of 12.9, 12.4, 13.2, 11.6 and 9.4 per cent for $^{91-92}$Sr, $^{92-93}$Y, ^{97}Zr, ^{140}Ba and ^{143}Ce respectively, from the thermal neutron fission of ^{233}U. If the range-velocity dependence involves the velocity to a power larger than unity, then the widths of the energy distribution as calculated from the widths of the range dispersion would be smaller than the quoted values of GOOD and WOLLAN(18) and PETRZHAK *et al.*(11) The values of PETRZHAK *et al.* are in good agreement with the value, 12.0 ± 0.8 per cent, reported by COHEN *et al.*(15) using a high resolution spectrometer and 12.2 per cent reported by MILTON and FRASER(17) using time of flight technique for the energy distribution of mass 97 fragments from the thermal neutron fission of ^{235}U. The values quoted have not been corrected for the dispersion resulting from prompt neutron evaporation from the initially excited fragments except for the value of MILTON and FRASER.(17)

The range distributions in aluminium of several fragments from the thermal neutron fission of ^{235}U have been determined and found to be approximately GAUSSIAN.[(20)] In the analysis of the present data, a Gaussian distribution is assumed for the straggling of the range, with straggling transverse to the original direction of flight of the fragment assumed to be negligible. For each range, Equation (1) is considered to be applicable, so that $F(t)/F(0)$ is given by

---

(13) J. LINDHARD and M. SCHARFF in R. B. LEACHMAN and H. ATTERLING, *Arkiv Fysik* **13**, 101 (1957).

(14) D. C. BRUNTON and G. C. HANNA, *Canad. J. Res.* **28 A**, 190 (1950).

(15) B. P. COHEN, A. F. COHEN, C. D. COLEY, *Phys. Rev.* **104**, 1046 (1956).

(16) W. E. STEIN, *Phys. Rev.* **108**, 94 (1957).

(17) J. C. D. MILTON and J. S. FRASER, *Canad. J. Phys.* **40**, 1626 (1962).

(18) W. M. GOOD and E. O. WOLLAN, *Phys. Rev.* **101**, 249 (1956).

(19) S. KATCOFF, J. A. MISKEL and C. W. STANLEY, *Phys. Rev.* **74**, 631 (1948).

(20) F. BROWN and B. H. OLIVER, *Canad. J. Chem.* **39**, 616 (1961).

$$\frac{F(t)}{F(0)}=\frac{\int_t^{\infty}(1-t/R)^2P(R)\,dR}{\int_0^{\infty}P(R)\,dR} \tag{10}$$

where $P(R)$ is defined by Equation (8) and $\rho = \lambda/2.355$ where λ is the ratio of the full-width at half-maximum to the mean range, R_0. $F(t)/F(0)$ is the ratio of the number of recoils found beyond a thickness t, to the total number of recoils escaping from one surface corrected for scattering and edge effects. Although $P(R)$ does not have the proper normalization for a set of range values from 0 to ∞, $P(R)$ may be regarded as exact since the contribution to the normalization integral of $P(R)$ for values from 0 to $-\infty$ is negligibly small in the cases considered. If a difference in the range-velocity dependence for the target and absorber is considered, Equation (10) is altered by raising t/R to the 0.97 power (see Sec. II. 4). Values of $F(t)/F(0)$ for various values of λ were obtained by numerical integration of Equation (10) for the observed fragments and plotted graphically as illustrated in Figs. 4 and 5 for ^{89}Sr and ^{99}Mo for a t value of 4.19 mg/cm^2. The two curves given in Figs. 4 and 5 are for $N_{\mathrm{U}}/N_{\mathrm{Al}}$ ratios of 0.97 and 1.00 (see Sec. II. 4). A value of λ for a given fragment was then interpolated from the graph corresponding to the observed value of $F(t)/F(0)$. Dispersion widths were also calculated from the thin target data[(1)] for thermal neutron fission of ^{235}U in a similar manner. Calculated values of $F(t)/F(0)$ for different values of λ were determined by the following expression

$$\frac{F(t)}{F(0)}=\frac{\int_{t+\omega}^{\infty}\left(1-\frac{t-\omega/2}{R}\right)P(R)\,dR+\frac{1}{2\omega}\int_t^{t+\omega}R(1-t/R)^2P(R)\,dR}{\int_0^{\infty}P(R)\,dR} \tag{11}$$

where ω is the target thickness equivalent mg/cm^2 Al, and $F(t)/F(0)$ is equal to $2F_t$ as reported by ALEXANDER and GAZDIK.[(1)] The first integral in the numerator corresponds to the ordinary thin target recoil equation. The second integral is a thick target type expression for the set of ranges $(t$–$t+\omega)$. The contribution to $F(t)/F(0)$ from this latter integral is negligible due to the relatively small value of ω.

The values of λ corresponding to the observed values of $F(t)/F(0)$ for both thick and thin targets are listed in Table 5, columns 5 and 8, respectively, for various fragments from the thermal neutron fission of ^{235}U. Widths for range distributions in aluminium measured directly[(12-20)] are also given in column 8 for comparison. The present results are in good agreement with this data.

The value of λ calculated for a given $F(t)/F(0)$ may be compared with an expected value calculated from the dispersion resulting from nuclear collisions of fragments of a given energy and that resulting from the energy distribution from the fission process If the two effects are considered to be independent and the distribution curve of each to be Gaussian, then

$$\lambda^2 = \frac{2}{3}k^2\left(\frac{R_N}{R_0}\right)^2 \frac{M_1M_2}{(M_1+M_2)^2} + \lambda^2_{\text{Fission}} \tag{12}$$

where k in the nuclear collision term is a constant (2 355) which converts ρ to λ The

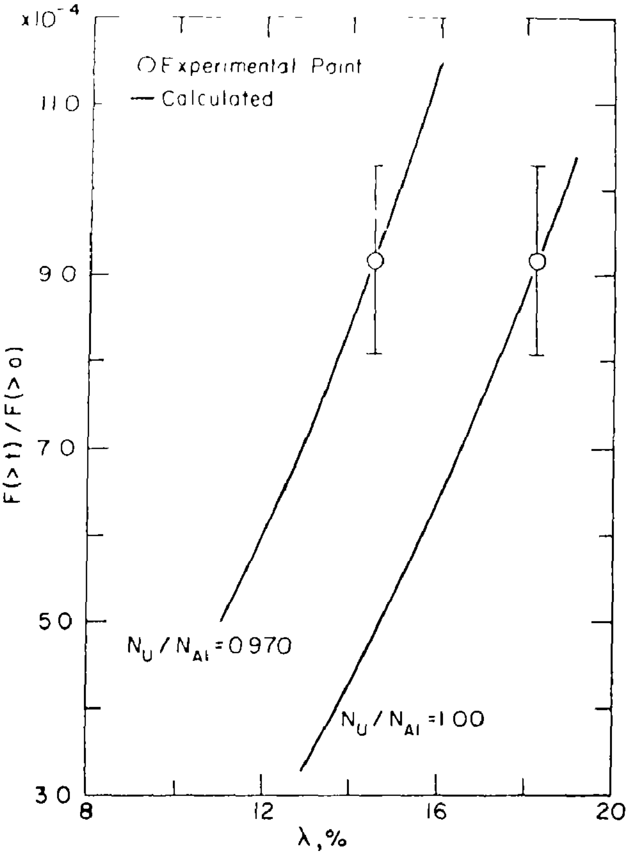


FIG 4 $\frac{F(>t)}{F(>0)}$ vs Range distribution width at half maximum for ^{89}Sr, for t = 4 19, mg/cm² Al, $\overset{\top}{\underset{\bot}{\circ}}$ Experimental Point, — Calculated curve

value of λ_{Fission} was taken to be one-half of the value of the energy distribution reported by PETRZHAK *et al*,[11] since the range is assumed proportional to the velocity Values for R_N/R_0 for aluminium were obtained by appropriate analysis of the dispersion measurements reported by PETRZHAK *et al*[11] and are about 0 09 0 1 in fair agreement with the ratios predicted by Bohr's expression[10] The values of λ calculated from Equation (12) are presented in Table 5, columns 6 and 9

Certain factors could affect the λ calculated for $F(>t)/F(>0)$ If the actual distribution is only approximately Gaussian and has a longer tail on the high range side as suggested by several investigators,[19,20] the number of recoils calculated for this foil will be less than the number of recoils observed for a given width and would be expected to be larger than that calculated for a Gaussian distribution. Although this enhanced probability on the high range side was not observed by PETRZHAK *et al.*,[11] nevertheless, allowing for such an occurrence, the effect should be small in the present case. The non-Gaussian behaviour reported[19,20] occurs at range values larger than 1.2R_0. The contribution to $F(>t)/F(>0)$ for ^{99}Mo and ^{89}Sr in the present case for range values greater than 1.2R_0 is small and approximately 10 per cent of the total for a 16 per cent dispersion width. Increasing the probability in this region by a factor of two, alters the calculated $F(>t)$ by 10 per cent and lowers the corresponding calculated λ by 3 per cent of its value.

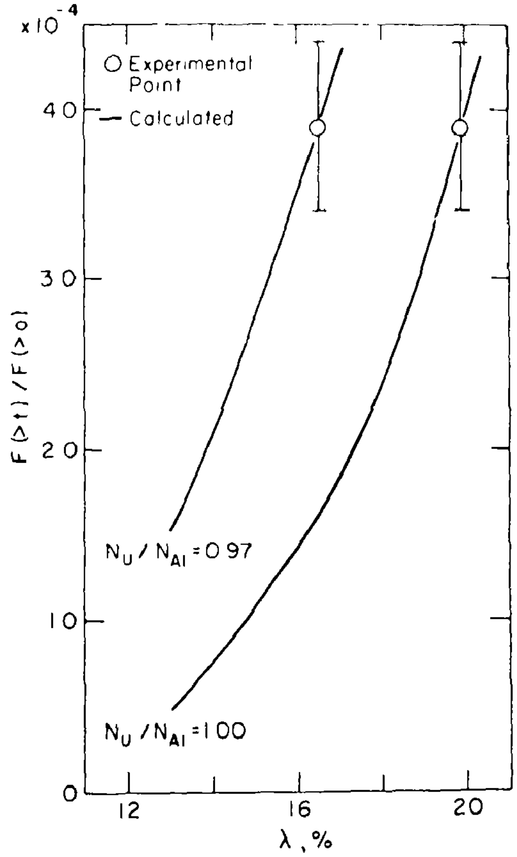


FIG. 5. $\frac{F(>t)}{F(>0)}$ vs. Range distribution width at half maximum for ^{99}Mo, for t = 4.19 mg/cm² Al. ⊥̄ Experimental Point, -- Calculated curve.

Non-uniformity in the foil thickness could also affect the present results. Calculations showed that if one-half the recoils traversed a thickness of aluminium 5 per cent less than the average thickness while the other half traversed a thickness 5 per cent greater than the average, the observed fraction of recoils could be accounted for by a Gaussian of 13 per cent full-width at half maximum. However, such a large variation in thickness is highly improbable in the present studies in which the aluminium thickness for 1 in. × 2 in. foils varied by less than 1 per cent.

TABLE 5.—FULL WIDTHS AT HALF-MAXIMUM FOR RANGE DISPERSION IN ALUMINIUM FOR VARIOUS FRAGMENTS FROM THERMAL NEUTRON FISSION OF ^{235}U

Nuclide	Thick target					Thin target			Reference
	t (mg/cm² Al)	R_{Al} (mg/cm²)	$F(t)/F(0)$	W(%) Obs	W(%) Calc.*	R_{Al} (mg/cm²)	W(%) Obs	W(%) Calc.*	
^{89}Sr	4.19	4.03	0.00092 0.00011‡	18.2 0.8	9.7				Present work
		4.12		14.5† 0.8					Present work
^{91}Sr						4.02	21 ± 4	9.6	(1)
^{97}Zr						3.99	15‡	9.6	(12)
						4.16	22**		(12)
^{99}Mo	4.19	3.86	0.00039 ≤0.00004‡	19.9 0.5	9.6				Present work
		3.96		16.5† 0.04					Present work
						4.16	22**	9.6	(12)
^{111}Ag						3.51	24 ± 3	9.4	(1)
^{115g}Cd						3.33	21 ± 1	9.3	(1)
^{131}I						3.37	18 ± 2	10.9	(1)
^{132}Te						3.34	18‡	10.9	(12)
						3.49	26**		(12)
^{136}Cs						2.64	17.7 ± 0.5	10.8	(20)
^{137}Cs						2.91	17.0 ± 0.5	10.8	(20)
^{140}Ba						2.82	17.5 ± 0.5	10.7	(20)

* Calculated from Equation (12)

† Dispersion width and range calculated by assuming different range-velocity dependence in Al and U

‡ Results obtained with uranium oxide target on a nickel backing

** Results obtained with uranium oxide target on a copper backing

± Estimate of cumulative experimental error

A least squares determination was then applied to the data to obtain the slope of the straight line into which the data developed. This slope yielded the mole ratio of water molecules to chelate molecules in the organic phase. The intercept of the straight line gave the solubility of water in the organic solvent at zero concentration of chelate.

EXPERIMENTAL

For the extraction of bis(8-quinolinol) dioxouranium(VI) into chloroform, the following procedure was followed.

To make up the concentration desired, a known amount of 0.0100 M dioxouranium(VI) nitrate was pipeted into a beaker containing a magnetic stirring bar. A given volume of water was added to the beaker followed by 0.1 N sodium hydroxide added dropwise until the pH was 8.8 ± 0.1 pH units as checked by a Beckman Model H pH meter. The resulting solution was then diluted to exactly 150 ml and transferred to a 500 ml separatory funnel. Exactly 150 ml of 0.033 M 8-quinolinol in chloroform solution was added to the funnel. The funnel was shaken 100 times and placed in a constant temperature bath at 25.0°C ± 0.1°C for exactly 15 min.

The funnel was then withdrawn from the water-bath and the excess water was wiped off from the funnel. The delivery tube was rinsed with dry acetone and the excess acetone was evaporated with a stream of dry air. This minimized the formation of emulsions which were due to water retained from the water bath.

Four 30 ml samples were then transferred to centrifuge tubes and centrifuged at 2000 rev/min for 60 sec. This served to remove any emulsified water. Care had to be taken not to continue the centrifugation any longer than 60 sec as heating of the samples resulted, which drastically decreased the solubility of water in the chloroform. It was found that no appreciable temperature change occurred in the first 90 sec and that the emulsified water was removed in about 30-45 sec. Thus 60 sec was deemed the optimum time of centrifugation.

A 25.00 ml sample was then pipeted from a 30 ml centrifuge tube and immediately transferred to the reaction beaker of the KF-3 Aquameter for titration with standard Karl Fischer Reagent. Because the Aquameter was equipped with 10 ml burettes, and the aliquot oftentimes required more than 10 ml of titrant, additional titrant was initially added from an auxiliary reservoir of Karl Fischer Reagent by means of a pipet.

While the first and succeeding samples were being titrated, the remaining centrifuge tubes were placed in the 25.0°C water bath to maintain temperature equilibrium.

The amount of dioxouranium(VI) nitrate added was adjusted such that the chelate concentration was in the range of 10^{-6}-10^{-5} moles of dioxouranium(VI) per 25.00 ml of chloroform. Usually a series of ten concentrations were used in each experiment providing forty individual titrations or forty raw values for each least squares determination.

It was important to note that in each experiment, a different order of concentrations was used in obtaining the raw values. This is, one time the least concentrated chelate solution was prepared and titrated first followed by the next most concentrated solution proceeding in order of increasing concentrations to the final concentration. Another time the order would be completely reversed and then random selection was used.

At least two and sometimes more solution blanks were prepared and titrated with each experiment. Usually one blank would be run initially and the second blank would be run after all of the chelate solutions had been prepared and titrated. This was not a strictly adhered to technique however. This was because there was usually no detectable difference between the blank solutions run at different times.

These two techniques would eliminate possible trends intentionally or unintentionally forming to induce artifacts.

Another procedure followed was the preparation of reagents. The usual method followed was to prepare each reagent freshly for each experiment with the exception of the standard metal ion solutions. This would preclude any error due to miscalculation of any concentrations.

RESULTS AND DISCUSSION

Bis(8-quinolinol) dioxouranium(VI) *extracted into chloroform*. The results of a typical experiment for this extraction system appear in Table 1 where the value X corresponds to the moles of uranium(VI) present per 25.00 ml of chloroform extractant times 10^{5}. The value Y corresponds to the number of moles of water per 25.00 ml of chloroform extractant times 10^{5}. Table 1 shows the calculation of the slope of the straight line obtained from the raw values. The intercept of this straight line is also

The present values for the widths obtained from thick target differential absorption measurements are in good agreement with those calculated from thin target differential measurements and those measured directly. However, they are a factor of 1.5 to 2 times the widths expected from measurements of range dispersion in gases.[11, 19]

Similar experiments for range dispersion were performed for ^{67}Cu, ^{89}Sr and ^{99}Mo from the 450 MeV proton fission of ^{238}U. The range, R, in Equation (11) is replaced by R_F or R_B in this case, where F and B refer to the forward and backward direction with respect to the proton beam, respectively. The average values of R_F and R_B determined from the simple expression, Equation (2), were found to be equal to $R_0 (1 \pm \eta_{\parallel})^{1.333}$ to within $\frac{1}{3}$ per cent, where R_0 is the average range and $\eta_{\parallel}$ is the ratio of the parallel component of the velocity of the struck nucleus to the velocity of the fragment as determined by more exact expressions involving R_0, $\eta_{\parallel}$, and N_{Al} (1.333), the velocity exponent in the range velocity expression for aluminium. Equation (2) was compared to a more exact expression describing $F(t)/F(0)$ in the region of the average values of R_F and R_B and it was found that the results agreed to within 1 per cent. The effect of a perpendicular component of the velocity of the struck nucleus has a negligible effect on $F(t)/F(0)$ in the present case because of its small value. The simple expression, Equation (2), may therefore be regarded as a good representation of the activity distribution in the aluminium catchers.

TABLE 6 — FULL-WIDTHS AT HALF-MAXIMUM FOR DISTRIBUTIONS OF R_F AND R_B FOR VARIOUS FRAGMENTS FROM THE 450 MeV PROTON FISSION OF ^{238}U

Nuclide	t (mg/cm² Al)	$\frac{I(t)}{I(0)}$	R_F or R_B (mg/cm² Al)	λ (%)	$\lambda_{\text{Fission}+\eta_{\parallel}}$ (%)
^{67}Cu	4.19	0.0211 ± 0.0021*	4.71 ± 0.01†	29 ± 6	22.8 ± 7.7
	4.19	0.0051 ± 0.0006	4.25 ± 0.01	25.5 ± 2.0	18.2 ± 3.0
			Average	27.2 ± 6.3	20.5 ± 8.3
^{89}Sr	4.21	0.00133 ± 0.00013	3.97 ± 0.01	24.3 ± 1.3	16.4 ± 2.2
	4.23	0.00033 ± 0.00004	3.69 ± 0.01	27.5 ± 0.5	20.9 ± 0.9
			Average	25.9 ± 1.4	18.6 ± 2.4
^{99}Mo	4.19	0.00029 ± 0.00004	3.72 ± 0.005	23.8 ± 0.6	15.7 ± 1.5

* Errors quoted are estimated of the cumulative experimental errors.
† Standard deviation from the mean.

The results for ^{67}Cu, ^{89}Sr and ^{99}Mo are presented in Table 6. The average value of λ is 25.6 ± 1.4 per cent which can be compared to the average value 19.0 ± 1.0 per cent for ^{89}Sr and ^{99}Mo from the thermal neutron fission of ^{235}U. If λ_{Fission} is equal to 6.4 per cent[11] in the thermal neutron case, λ_{Al} for straggling in aluminium is found to be 17.9 ± 1.0 per cent. The observed values of λ for fragments from the proton fission of ^{238}U were corrected for straggling in aluminium and the calculated λ for fission and $\eta_{\parallel}$ are presented in the final column of Table 6. The average value of $\lambda_{\text{Fission}+\eta_{\parallel}}$ is 18.3 ± 2.0 per cent.

The relatively large value of $\lambda_{\text{Fission}+\eta_{\parallel}}$ in the proton fission of ^{238}U may be expected to result from several sources. First, there is a distribution of the nuclides undergoing fission varying in charge number and mass as a result of the nuclear cascade process and neutron evaporation competition. Second, there is also an effect arising from neutron evaporation from the parent fragment during its time of flight. Third, $\lambda_{\text{Fission}, \eta_{\parallel}}$ contains a contribution from the distribution of $\eta_{\parallel}$. Due to the relatively small average value of $\eta_{\parallel}$ (0.03), the contribution to $\lambda_{\text{Fission}, \eta_{\parallel}}$ should be small. Fourth, a relatively large spread in $\lambda_{\text{Fission}, \eta_{\parallel}}$ as compared to λ_{Fission} for the thermal neutron case may originate in a large spread in the kinetic energy release for a given fragment arising from the fission process, resulting from the

TABLE 7—THICK TARGET RANGE MEASUREMENTS FOR VARIOUS FISSION FRAGMENTS FROM U, Bi AND Ta

Fission fragment	Ranges (mg/cm²)* Target	Aluminium	$R(\text{target})/R_{\text{Al}}$
	Thermal neutron fission of ^{235}U		
^{89}Sr	10.92 ± 0.02†	4.03 ± 0.01	2.71 ± 0.01
^{99}Mo	10.63 ± 0.02	3.86 ± 0.01	2.75 ± 0.01
^{115g}Cd	9.12 ± 0.02	3.29 ± 0.01	2.77 ± 0.01
	450 MeV proton fission of ^{238}U		
^{67}Cu	11.88 ± 0.02	4.49 ± 0.01	2.65 ± 0.01
^{89}Sr	10.43 ± 0.02	3.83 ± 0.01	2.72 ± 0.01
^{99}Mo	9.78 ± 0.04	3.58 ± 0.01	2.73 ± 0.01
^{115g}Cd	9.15 ± 0.02	3.32 ± 0.01	2.76 ± 0.01
^{115m}Cd	8.67 ± 0.03	3.15 ± 0.01	2.75 ± 0.01
	450 MeV proton fission of Bi^{209}		
^{67}Cu	10.47 ± 0.03	4.00 ± 0.004	2.62 ± 0.01
^{99}Mo	8.37 ± 0.02	3.09 ± 0.004	2.71 ± 0.01
^{115g}Cd	7.89 ± 0.02	2.89 ± 0.008	2.73 ± 0.01
^{115m}Cd	7.39 ± 0.02	2.71 ± 0.008	2.73 ± 0.01
	450 MeV proton fission of ^{181}Ta		
^{67}Cu	8.94 ± 0.03	3.48 ± 0.01	2.57 ± 0.01
^{91}Sr	7.04 ± 0.02	2.68 ± 0.01	2.63 ± 0.01
^{99}Mo	6.63 ± 0.02	2.48 ± 0.01	2.67 ± 0.01

* Ranges have been corrected for scattering and edge effects.

† Standard deviation from the mean.

numerous fission modes available at high excitation energies and from a large spread in the excitation energy of the fission nuclides.

3. *Relative ranges in* Ta, Bi *and* U *for fission fragments*

Fission fragment ranges in U, Bi and Ta and corresponding ranges in aluminium are given in Table 7. The ranges have been corrected for the scattering and edge effects as discussed in Section II, 1 and include corrections for the velocity of the struck nucleus and the anisotropy of the fission fragment. The ratio of the range in the target to that in aluminium is also tabulated. These ratios can be expressed by the following equations for the fragment studied ranging from ^{67}Cu to ^{115}Cd for the energy region 0.75–1.5 MeV/amu:

$$R_{\text{U}}/R_{\text{Al}} = 2.507 + 0.002282A \tag{13}$$

$$R_{\text{Bi}}/R_{\text{Al}} = 2.477 + 0.002282A \tag{14}$$

$$R_{\text{Ta}}/R_{\text{Al}} = 2.434 + 0.002282A \tag{15}$$

where A is the mass number of the fragment. The ranges in aluminium used are those determined by the thick target-thin absorber method and are 1–2 per cent less than values determined with a thin target (see Table 1). If the ratio of the range in the target to that in aluminium is normalized, for a given fragment, to that for uranium the resulting values represent the relative ranges of fragments in Bi and Ta compared to uranium. The results are presented in Table 8. The average values for Bi and Ta are 0·989 ± 0·010 and 0·971 ± 0·010 respectively.

From BOHR's range–velocity relation(2) for fission fragments stopping in matter, the ratio of ranges (mg/cm^2) of a given fragment for two different stopping materials is given approximately by

$$R_1/R_2 \approx (A_1/A_2)(Z_2/Z_1)^{1/3}$$

where the subscripts 1 and 2 refer to the different materials, and A, Z and R represent the mass number, the atomic number, and the range respectively. For Bi and Ta with respect to uranium, the calculated values are 0·909 and 0·822, 8 and 15 per cent, respectively, lower than the experimental values.

TABLE 8—COMPARISON OF RANGE RATIOS OF U, BI AND TA WITH RESPECT TO Al

Nuclide	U	Bi	Ta
^{67}Cu	2·65 (1·00)*	2·62 (0·989)	2·57 (0·970)
^{89}Sr	2·71 (1·00)		2·63† (0·970)
^{99}Mo	2·74 (1·00)	2·71 (0·989)	2·67 (0·974)
^{115,115m}Cd	2·76 (1·00)	2·73 (0·989)	

* Values in parenthesis refer to normalization with respect to ratio for uranium.

† Refers to value for ^{91}Sr.

The range ratios in Table 7 are lower than the previously observed values for these ratios with Bi and Au as the heavier stopping material. For ^{91}Sr and ^{129,133m}Ba, from the 450 MeV proton fission of a thick bismuth target (~40 mg/cm^2) SUGARMAN *et al.*(1) have observed range ratios of bismuth to aluminium of 2·9 ± 0·1 and 2·8 ± 0·2 respectively. The bismuth and aluminium range measurements have not been corrected for scattering and edge effects (the latter is insignificant in this case). A 4 per cent correction for scattering would lower the range ratio by 6 per cent in reasonable agreement with the present data. For ^{97}Zr from the thermal neutron fission of a thin uranium target, SUZOR(12) has reported a value for the range ratio of Au to Al of 2·73 ± 0·15. This value is in good agreement with that expected for Au from these studies. Employing an ionization chamber to determine the recoil activity occurring beyond a given thickness of absorber SEGRÈ and WIEGAND,(21) observed a value of 3·0 for the range ratio of gold to aluminium for the gross products from the neutron fission of a thin uranium target. The ranges represent extrapolated ranges and therefore contain significant errors from the extrapolation as well as inherent experimental errors in the method, making a significant comparison with the present results difficult.

4. *Comparison of ranges in aluminium measured with thin and thick targets*

Ranges in aluminium for various fragments from the thermal neutron fission of uranium determined by the thin target technique may be compared with experimental and calculated values obtained with a thick uranium target in Table 9. The experimental values are from Table 7 and the calculated values were obtained by correcting ranges in uranium for scattering and edge effects from Fig. 1 and Table 4 and then

TABLE 9. RANGES OF FRAGMENTS FROM THE THERMAL NEUTRON FISSION OF ^{235}U

Observed nuclide	Ranges in uranium (mg/cm²)	Ranges in aluminium (mg/cm²) Thick target	Ranges in aluminium (mg/cm²) Thin target	Reference
^{83}Br			4.05 ± 0.03	(23)
^{89}Sr	10.92 ± 0.02*	4.03 ± 0.01*	4.12 ± 0.02	(1)
	10.97 ± 0.02$^{(2)}$	4.05 ± 0.02 (calc)	3.74	(22)
^{91}Sr	10.97 ± 0.04$^{(2)}$	4.05 ± 0.02 (calc)	4.02	(1)
^{95}Zr	10.81 ± 0.03$^{(2)}$	3.97 ± 0.02 (calc)	3.64	(22)
^{97}Zr	10.81 ± 0.02$^{(2)}$	3.97 ± 0.02 (calc)	3.99 ± 0.15†	(12)
			4.16 ± 0.15‡	(12)
^{99}Mo	10.63 ± 0.02*	3.86 ± 0.01*	4.16 ± 0.15‡	(12)
	10.64 ± 0.02$^{(2)}$	3.89 ± 0.03 (calc)		
^{103}Ru	10.65 ± 0.07*	3.89 ± 0.03 (calc)	3.57	(22)
	10.76 ± 0.04$^{(2)}$	3.93 ± 0.02 (calc)		
^{111}Ag	9.32 ± 0.06$^{(2)}$	3.38 ± 0.02 (calc)	3.51 ± 0.02	(1)
^{115}Cd	9.12 ± 0.02*	3.29 ± 0.01*	3.33 ± 0.04	(1)
	9.12 ± 0.03$^{(2)}$	3.29 ± 0.02 (calc)		
^{129m}Te	9.33 ± 0.08*	3.34 ± 0.03 (calc)	3.34	(22)
	9.39 ± 0.02$^{(2)}$	3.36 ± 0.01 (calc)		
^{131}I			3.16	(22)
			3.37 ± 0.02	(1)
^{132}Te	9.28 ± 0.03*	3.31 ± 0.02 (calc)	3.34 ± 0.15†	(12)
	9.28 ± 0.02$^{(2)}$	3.31 ± 0.01 (calc)	3.49 ± 0.15‡	(12)
^{136}Cs	8.07 ± 0.03$^{(2)}$	2.87 ± 0.02 (calc)	2.64 ± 0.01	(20)
^{137}Cs	8.86 ± 0.03$^{(2)}$	3.15 ± 0.02 (calc)	2.91 ± 0.01	(20)
^{137}I			3.21 ± 0.04	(23)
^{140}Ba	8.44 ± 0.03$^{(2)}$	2.99 ± 0.01 (calc)	2.98 ± 0.01	(1)
			2.82 ± 0.01	(20)
			2.75	(22)
^{141}Ce	8.27 ± 0.01$^{(2)}$	2.93 ± 0.01 (calc)	2.69	(22)
^{144}Ce	8.06 ± 0.07$^{(2)}$	2.85 ± 0.03 (calc)	2.54	(22)

* Present work.

† Results obtained with uranium oxide layer on nickel backing.

‡ Results obtained with uranium oxide layer on copper backing.

employing the ratios found in Equation (13), to convert the corrected ranges in uranium to ranges in aluminium. With the exception of ^{111}Ag, good agreement is found between the thick target values and the thin target values reported by ALEXANDER and GAZDIK$^{(1)}$ and the values reported by SUZOR$^{(12)}$ from measurements with thin uranium oxide targets on a nickel backing. The ranges reported by BROWN and OLIVER$^{(20)}$ and FINKLE *et al.*$^{(22)}$ appear lower than the other reported ranges by

---

(21) F. SEGRÈ and C. WIEGAND, *Phys. Rev.* **70**, 808 (1946).

(22) B. FINKLE, E. J. HOAGLAND, S. KATCOFF, N. SUGARMAN, "*Radiochemical studies: the fission products*", (Edited by C. D. CORYELL and N. SUGARMAN) NNES Div. IV, Vol. 9, Book 1, pp. 463–471, McGraw-Hill, New York (1951).

(23) N. SUGARMAN, *J. Chem. Phys.* **15**, 544 (1947).

approximately constant factors in each case, suggesting a possible inherent experimental error in thickness measurements of the absorbers or in corrections for velocity losses in the target

There appears to be a consistent difference in the aluminium ranges in Table 1 for the thick and thin target methods, the thick target ranges being somewhat lower than those observed with a thin target [(1)] If this effect is outside the experimental error, the apparent difference can be accounted for by considering different range-velocity dependencies in the target and catcher materials If the range (R) velocity (V) expression for a stopping material (i) is given by

$$R_i = k_i V^{N_i}$$

a recalculation of the differential expression for a thick target yields

$$\frac{F(t)}{F(0)} = [1 - (t/R_{Al})^{N_U/N_{Al}}]^2 \qquad (16)$$

The ratios of N_U/N_{Al} found for ^{89}Sr and ^{115g}Cd to give ranges in aluminium the same as those determined with a thin target was 0·870 ± 0·003 For N_{Al} equal to $\frac{3}{2}$ N_U is equal to 1·293

5 *Conclusions*

Ranges in aluminium of ^{89}Sr and ^{115g}Cd from the thermal neutron fission of ^{235}U were determined by the thick target differential recoil method and agree with ranges determined by the thin target differential method to within 1–2 per cent The agreement depends upon the application of corrections for scattering and edge effects in the thick target method and for target thickness in the thin target case The edge effect has satisfactorily accounted for differences in uranium ranges obtained with 1 mil and 3 mil uranium targets for a number of fission fragments Moreover scattering and edge corrections applied to the data from the 450 MeV proton fission of bismuth eliminated an apparent dependence of the average range in aluminium on the thickness of the first aluminium catcher used in the range measurement The 1–2 per cent remaining difference between the thick and thin target range measurements in aluminium may be attributed to a difference in the range velocity dependence in uranium and in aluminium However such a difference in the range–velocity dependence between the heavier target material and aluminium was not needed to explain the bismuth range results Consequently the difference in the range-velocity dependence for uranium and aluminium is not definitely established

Range dispersion widths in aluminium based on a Gaussian distribution of ranges, have been calculated for fragments from the thermal neutron fission of ^{235}U and the 450 MeV proton fission of ^{238}U The values obtained with a thick target for the thermal neutron case are in agreement with values calculated from thin target differential experiments and dispersion widths measured experimentally with thin targets An average value of the full width at half maximum of 19·0 ± 1·0 per cent for the range dispersion in aluminium was obtained for ^{89}Sr and ^{99}Mo in the thermal neutron experiments The range dispersion widths in aluminium are a factor of 1·5 to 2 times greater than values calculated from dispersion widths determined with gases If the range dispersion width from the fission process is 6·4 per cent in the thermal neutron case, the range dispersion width from the straggling of fission fragments in aluminium is calculated to be 17 9 ± 1 0 per cent in the thick target experiments The average dispersion width is 25 6 ± 1 9 per cent, for ^{67}Cu, ^{89}Sr and ^{99}Mo from the 450 MeV proton fission of ^{238}U The average dispersion width in the high energy case, corrected for straggling in aluminium, is 18 3 ± 2 0 per cent

The large increase in the width of 18 3 per cent as compared to that of a fragment from thermal neutron fission of 6 4 per cent can be attributed to several sources arising from high energy fission First, there are a variety of nuclides resulting from the nuclear cascade process and neutron evaporation competition which undergo fission as compared to the single fissioning nucleus in the thermal neutron case Second, there is a much broader spectrum in the number of neutrons evaporated from the parent fragment during its time of flight in the high energy process Third, there is a spread in the range arising from a distribution in the velocity imparted to the struck nucleus (The contribution from this source, however, should be small) Finally, an increase in the width from the fission process could result from an increase in the number of fission modes available in the high energy case as a result of the higher excitation energy deposited in the fissioning nucleus and the broad spectrum of excitation energy induced by the bombardment

The ratio of the range in the target material to that in aluminium for U, Bi and Ta targets for a given fission fragment has been found to vary by 3 per cent from uranium to tantalum The variation in the ratio expected from the range-velocity expression given by Bohr is 15 per cent A general expression for converting ranges in heavy elements in this region to ranges in aluminium has been presented

J Inorg Nucl Chem , 1963, Vol 25 pp 1343 to 1350 Pergamon Press Ltd Printed in Northern Ireland

THERMAL NEUTRON CAPTURE IN GASEOUS AND LIQUID PHOSPHINES—II

NON-VOLATILE PRODUCTS, PRIMARY RETENTION AND SCAVENGER EFFECTS*

M HALMANN and L KUGEL
Isotope Department The Weizmann Institute of Science, Rehovoth, Israel

(*Received* 26 *March* 1963 *in revised form* 22 *April* 1963)

Abstract ^{32}P-labelled products from the thermal neutron capture in gaseous and liquid trimethylphosphine have been determined using gas and paper chromatography and paper electrophoresis Inclusion of substances which might act as radical scavengers had no effect on product yields The amount of primary retention of ^{32}P in trimethylphosphine was found to be of the same order of magnitude as predicted by the "random walk theory" The yields of labelled compounds increase in the series trimethyl-, dimethyl, methyl- and inorganic ^{32}P products The yields of di- and trimethylphosphine after neutron capture in gaseous trimethylphosphine are less than predicted by simple statistical considerations, while higher yields than predicted are obtained from liquid trimethylphosphine

THE volatile ^{32}P-containing products formed after radiative thermal neutron capture [^{31}P$(n,\gamma)^{32}$P reaction] in gaseous trimethylphosphine have been shown to be phosphine methyl-, dimethyl- and trimethylphosphine[1] The non-volatile products formed during pile irradiation, and deposited on the walls of the quartz containers, have now been identified

RESULTS

Gas phase irradiations

Preliminary experiments indicated that the aqueous washings of the quartz tubes contained both lower and higher oxidation states of phosphorus oxyacids Not all these acids could be resolved by a single method of analysis, but a complete resolution could be obtained by a combination of paper-chromatography and -electrophoresis,[2] both on the original aqueous washings of the quartz tubes, and after its oxidation with bromine water Results for the analysis of one irradiation experiment are given in Figs 1 and 2 Most of the ^{32}P-containing acids were easily identified by simultaneous chromatography runs of the inactive acids The large peak at about R_F = 0.53 in the paper chromatography of the original aqueous washings of the walls (see Part a of Fig 1) disappeared after oxidation with bromine water (see Part b) The expected phosphorus oxyacids having R_f values in this range are hypophosphorous acid, H_3PO_2, and dimethylphosphinic acid Me_2PO_2H However the ^{32}P-activity of this fraction (33 per cent of the total activity) was larger than the sum of

---

* This study is part of a thesis submitted by L Kugel to Technion Israel Institute of Technology in partial fulfilment of the requirement for the degree of M Sc

[1] M HALMANN, *Proc Chem Soc* 289 (1960) and "*Chemical Effects of Nuclear Transformations*", Proceeding of a Symposium by the International Atomic Energy Agency, Prague 1960 published in Vienna, 1961, p 197, are to be considered Part I

[2] M HALMANN and L KUGEL *Bull Res Council Israel* **10** A, 124 (1961) L KUGEL and M HALMANN, *Ibid* **11** A, 205 (1962)

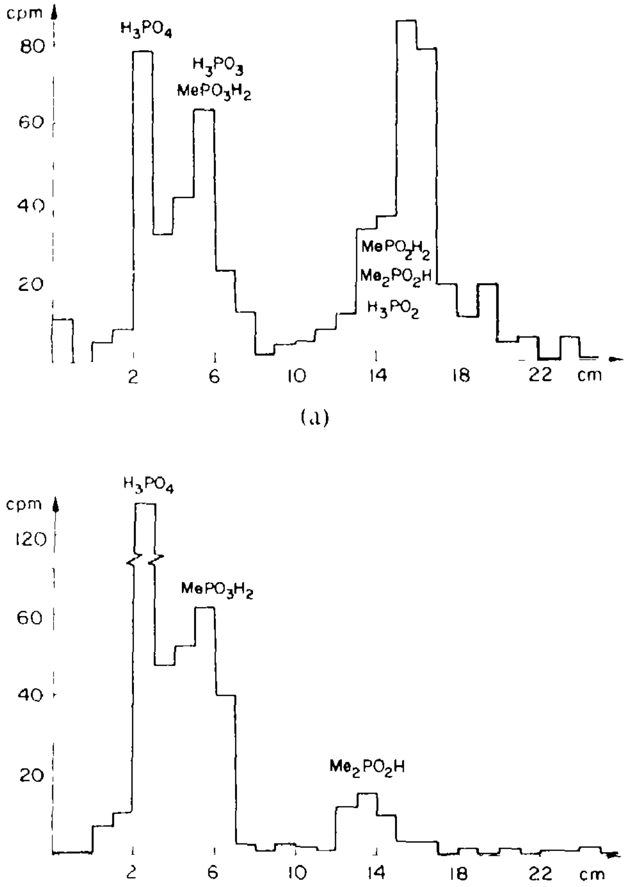


FIG. 1 Paper chromatography (ascending in n-propanol, ammonia, water 6 3 1) of wall activity after neutron activation of Me_3P (a) Without oxidation (b) After oxidation with bromide water

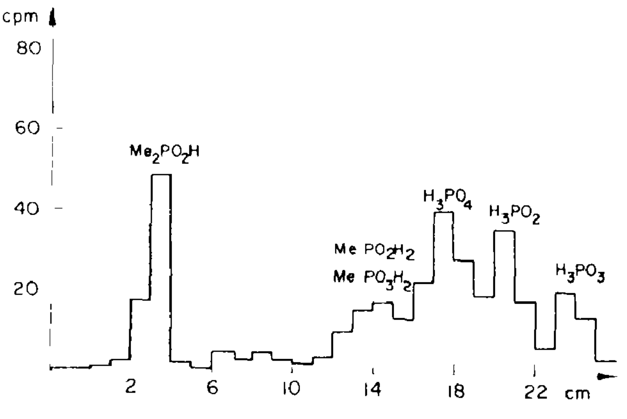


FIG. 2 - Paper electrophoresis (in 0.1N lactic acid at 8.5 V cm^{-1} for 3 hr) of wall activity after neutron activation of Me_3P

activities of these two acids, determined separately by paper electrophoresis (see Fig. 2). The difference in activity (about 12 per cent) was predicted to be due to *methylphosphinic acid*, Me(H)PO$_2$H. This compound was therefore synthesized[3] and its behaviour in paper chromatography and electrophoresis (before and after oxidation with bromine water) fitted that of the unexpected ^{32}P-activity. Results for several runs are given in Table 1. Trimethylphosphine oxide and pyrophosphoric acid were not formed in appreciable yield in these experiments.

TABLE 1.—YIELD PER CENT OF ^{32}P-CONTAINING PRODUCTS AFTER NEUTRON IRRADIATION IN THE THERMAL COLUMN AT 2×10^{10} NEUTRON CM^{-2} SEC^{-1}

Run no.	1	2	3	4	5	6	7
Me$_3$P(mm Hg)	204	146	84	38	14	3	Liquid, −78
Irradn. (hr)	3	3	6	25	25	78	3
PH$_3$	26.8	30.4	32.1	26.9	26.1	3.8	5.8
MePH$_2$	1.8	5.3	2.2	4.1	2.3	2.4	5.3
Me$_2$PH	0.6	2.2	1.9	2.5	1.9	2.1	4.7
Me$_3$P	0.5	0.6	0.4	0.7	0.6	0.4	3.0
H$_3$PO$_4$		14.5					8.5
H$_3$PO$_3$		6					6.5
H$_3$PO$_2$		11.5					10.0
H$_4$P$_2$O$_7$							1.2
MePO$_2$H$_2$		11.5					24.5
MePO$_3$H$_2$		9					4.0
Me$_2$PO$_2$H		9					21.0
Me$_3$PO							5.5
Total non-volatile activity	70.3		63.4	62.9	69.2	61.2	

Liquid phase irradiations

At the temperature of a dry-ice acetone bath (−78°) trimethylphosphine is mainly in the liquid phase (the freezing point is −84.5°). As shown in Table 1 (Run No. 7), the main effect of irradiation at −78° compared with irradiation at room temperature is in the considerably enlarged yield of Me(H)PO$_2$H, Me$_2$PO$_2$H, Me$_3$P, Me$_3$PO and pyrophosphoric acid. The increases in yield are mainly at the expense of phosphine and orthophosphoric acid.

Scavenger experiments

Attempts to find scavengers for free radical reactions during neutron capture in trimethylphosphine are described in Table 2. Runs 19 and 20 were made on trimethylphosphine mixed with small amounts of either 1-butene or trimethylamine (containing 20 per cent dimethylamine). In neither case was any marked change in the yields of the volatile products observable compared with results in pure trimethylphosphine (Run No. 1). Many irradiation experiments were also made on mixtures of trimethylphosphine and methane, but the ^{32}P distribution in the products was of poor reproducibility. Attempts to ascribe these effects to scavenger action of trace impurities of oxygen or water were not successful.

---

[3] D. Hiat, M. Halmann, L. Kugel and J. Reuben *J. Chem. Soc.* 3837 (1962).

TABLE 2. SEARCH FOR SCAVENGER EFFECTS DURING IRRADIATION IN THE THERMAL COLUMN

Gas mixture			PH_3	$MePH_2$	Me_2PH	Me_3P	Non-volatile products
Run no.	Me_3P mm Hg	Added gas mm Hg					
1	204	–	26.8	1.8	0.6	0.5	70.3
19	194	1-Butene 4 mm	29.8	3.6	1.4	0.9	64.3
20	196	Me_3N Me_2NH 2.7 mm	30.4	3.7	3.2	1.3	61.4

TABLE 3.—YIELD PER CENT OF ^{32}P-CONTAINING PRODUCTS WITH CHANGE IN PARENT (TARGET) COMPOUND

Run no.	Target (mm Hg)	Added gas	mm Hg	Water mm Hg	Products				
					PH_3	$MePH_2$	Me_2PH	Me_3P	Non volatiles
29	Me_3P, 4.8	H_2	410	-	62.3	1.1	0.1	0.05	36.5
27	PH_3, 5.5	CH_4	550		48.6	3.6	0.3	0.2	40.0
28	PH_3, 5.7	CH_4	670	0.8	45.0	10.0	0.7	0.8	43.5

Variation of target compound

In all the irradiations described in Tables 1 and 2, the target compound was trimethylphosphine. The ^{32}P-labelled trimethylphosphine isolated after irradiation may therefore be due either to primary retention or to some recombination reaction of a recoiling "free" phosphorus atom. Similarly, the ^{32}P labelled dimethylphosphine and methylphosphine may be due to partial retention. The experiments described in Table 3 were carried out to test this possibility. In Run No. 29 trimethylphosphine mixed with a large excess of hydrogen was irradiated, and yielded only 0.05 ± 0.05 per cent of ^{32}P in the Me_3P fraction. In this experiment reactions of free phosphorus atoms to reform methyl-phosphorus bonds are improbable and the results provide an upper limit of 0.1 per cent for the primary retention.

Runs Nos. 27, 28 are the inverse experiment. Here phosphine was irradiated in a large excess of methane. Since no methylphosphines were originally present, the yields of ^{32}P-labelled methyl, dimethyl- and trimethyl-phosphine must be due solely to reactions forming these compounds. For some yet unknown reason, the addition of traces of water during the irradiation seems to enhance the yields of methylphosphines. In Runs 27 and 28 the yields of methylphosphines are of the same order of magnitude as in irradiations of trimethylphosphine, this proves that essentially products are due to recombination and that failure of bond-breakage during neutron capture in gaseous phosphines is negligible.

DISCUSSION

While the volatile ^{32}P-containing products of thermal neutron capture in trimethylphosphine were determined by gas chromatography in a helium atmosphere(1) and may thus be the original stable chemical forms obtained after recoil of ^{32}P nuclei the non-volatile products were determined in the presence of air. Almost all th *calculated in Table 1. This value corresponds to the solubility of water in t chloroform blank*

The value obtained from Table 1 indicates 5.2 moles of water associated with each mole of uranium(VI) in the extracted phase. The mean of three independent experiments was 5.3 ± 1.8 moles of water per mole of uranium(VI).

Neither the dioxouranium(VI) ion nor the 8-quinolinol compound reacted with the Karl Fischer Reagent.[2]

TABLE 1. LEAST SQUARES DETERMINATION OF THE NUMBER OF WATER MOLECULES ASSOCIATED WITH BIS(8-QUINOLINOL) DIOXOURANIUM (VI) TRIAL 1

Sample	X	Y	(X)(Y)	(X)^2
1	0.00	191	0.0	0.0000
2	0.00	186	0.0	0.0000
3	0.00	192	0.0	0.0000
4	0.00	189	0.0	0.0000
5	0.00	193	0.0	0.0000
6	0.00	193	0.0	0.0000
7	0.00	192	0.0	0.0000
8	0.00	186	0.0	0.0000
9	0.17	191	32.5	0.0289
10	0.17	206	35.0	0.0289
11	0.17	193	32.8	0.0289
12	0.17	192	32.6	0.0289
13	0.29	191	55.4	0.0841
14	0.29	190	55.1	0.0841
15	0.29	204	59.1	0.0841
16	0.29	186	53.9	0.0841
17	0.40	221	88.4	0.1600
18	0.40	193	77.2	0.1600
19	0.40	193	77.2	0.1600
20	0.40	186	75.2	0.1600
21	0.57	191	108.9	0.3249
22	0.57	191	108.9	0.3249
23	0.57	188	101.7	0.3249
24	0.57	194	110.6	0.3249
$n = 24$	5.72	4632	1104.5	3.3916

$$\text{Slope} = \frac{(n)\Sigma(X)(Y) - \Sigma(X)\Sigma(Y)}{(n)\Sigma(X^2) - \Sigma(X)^2}$$

$$= 5.2$$

$$\text{Intercept} = \frac{\Sigma(X^2)\Sigma(Y) - \Sigma(X)\Sigma(X)(Y)}{(n)\Sigma(X^2) - \Sigma(X)^2}$$

$$= 192$$

It was noted that the chelate apparently dissociated after a certain number of hours. This was confirmed through spectrophotometric analysis of the chelate solutions with respect to time. An aqueous dioxouranium(VI) nitrate solution was observed to undergo some sort of hydrolysis also after a period of several hours standing. This was accomplished by a drop in the pH value indicating an hydrolysis mechanism. This may be directly related to the chelate instability as well.

Because of the chelate breakdown with time, the half-life of the water-chelate association could not be followed. Apparently, the water was there as long as the

^{32}P containing products identified on the walls of the irradiation tube were phosphorus oxyacids, yet we do not know whether the oxidation occurred already during the process of "cooling down" of the recoiling ^{32}P atom, or only after opening the tube to air. Although the tubes used had been degassed prior to irradiation to a pressure of 10^{-5} mm Hg, the number of oxygen atoms from water and air remaining at this pressure (about 10^{13}) is of the same order of magnitude as the number of ^{32}P atoms produced.

One possible reactive intermediate is the molecule $H-C\equiv P$.(4) Its reactions may account for some of the observed ^{32}P-products, such as

$$CH_3PH_2, \qquad CH_3P(H)(O)(OH) \quad \text{and} \quad CH_3PO_3H_2$$

A hypothetical intermediate for dimethylphosphorus derivatives could be $(CH_2)_2P$, the positive ion of which was found in the mass spectrum of trimethylphosphine.(5)

The yield of ^{32}P in the parent fraction after irradiation in the liquid phase at -78° (Run No. 7) is similar to that obtained from liquid tri-n-butyl phosphate,(6) a large fraction of which was considered to be due to primary retention.

Scavengers

In studies of chemical effects of nuclear recoil of halogen, tritium or carbon atoms, a variety of "radical scavengers" have been discovered, the presence of traces of which during irradiation prevented the formation of part of the radiochemical products. The "scavenged" fraction, the part which is thus prevented from being formed, is generally considered to be due to reactions of atoms or radicals in the thermal energy range. No such scavengers have been prescribed for phosphorus atoms, and it was therefore necessary to search for suitable compounds. Halogen or oxygen molecules are often used in other systems, but could not be used with trimethylphosphine, because they would immediately be consumed forming trimethylphosphine dihalides, or trimethylphosphine oxide. Nitric oxide was tried, but was found also to react rapidly with trimethylphosphine.(7)

A pronounced scavenger effect of cyclohexane was observed for the neutron irradiation of phosphorus trichloride, but was ascribed to scavenging of free chlorine atoms.(8) We found that 1-Butene had no appreciable effect on the yields of ^{32}P-containing products from gaseous trimethylphosphine (see Run 19 in Table 2).

Distribution of recoil products

It is possible to divide the ^{32}P labelled products after neutron irradiation of trimethylphosphine into four groups depending on the number of methyl-phosphorus bonds which they contain. This distribution is different for products formed after irradiation in the gas phase (see second column of Table 4) or in the liquid phase

(4) T. E. Gier, *J. Amer. Chem. Soc.* **83**, 1769 (1961).

(5) M. Halmann, *J. Chem. Soc.* 3270 (1962).

(6) K. E. Siekierska, A. Halpern and A. Siuda, *Nukleonika* **5**, 635 (1960); *Chemical Effects of Nuclear Transformations*, Proceedings of a Symposium by the International Atomic Energy Agency, Prague 1960, published in Vienna 1961, p. 171. I. G. Campbell, A. Poczynajło and A. Siuda, *J. Inorg. Nucl. Chem.* **10**, 225 (1959). A. Siuda, *Nukleonika* **7**, 623 (1962).

(7) M. Halmann and L. Kugel, *J. Chem. Soc.* 3272 (1962).

(8) H. Drawe and A. Henglein, *Z. Naturforsch.* **17 b**, 486 (1962).

(third column). The first-row includes all inorganic products-phosphine and inorganic phosphorus oxyacids, the second row includes methylphosphine and all methylphosphorus oxyacids, etc.

It is possible to make a rough prediction of the distribution of yields to be expected in dilute gaseous phase, by assuming that hot ^{32}P atoms have equal affinity for becoming attached to hydrogen or carbon atoms on colliding with trimethylphosphine molecules. Since the number of hydrogen atoms is three times that of the carbon atoms, and neglecting the differences in atomic diameters or scavenger effects of impurities the distribution expected by purely statistical considerations is that given in the fourth column of Table 4. The yields of organophosphorus products after gas phase irradiation was always less than predicted. After liquid phase irradiation, the yields of di- and trimethylphosphorus products were higher than predicted. The preference for inorganic products from gas phase irradiations may be explained by scavenger effects of some unknown trace impurities or by a preference of abstraction of a hydrogen atom rather than a methyl group, since the carbon atoms are in part screened by hydrogen atoms. The increased organophosphorus yields in the liquid phase irradiation seem understandable as effects of a cage of free methyl radicals in the vicinity of the hot phosphorus atom.

TABLE 4. DISTRIBUTION OF METHYL PHOSPHORUS-32 CONTAINING PRODUCTS

No. of P–C bonds in products	Yield from gas phase irradiation (%)	Yield from liquid phase irradiation (%)	Yield calculated by statistical model (%)
0	62.4	32.0	42.2
1	25.8	33.8	42.2
2	11.2	25.7	14.1
3	0.6	8.5	1.5

Primary retention

The problem of the extent of primary retention following neutron capture in phosphorus compounds has been subject to considerable discussion.(1,6,8,9) The observed yield of ^{32}P in the parent compounds after neutron irradiation of liquid(6) or solid(9) phosphorus compounds was always more than 2–5 per cent of the total activity. To account for these results, a theory has been developed(10) which makes it possible to predict the probability of partial cancellation of momenta of oppositely directed γ-rays of the γ-cascade following thermal neutron capture. Assuming the cascade to be emitted simultaneously as three equal γ-quanta with random angular correlation, a simplified formula was proposed(10) for the probability P of failure of bond breakage,

$$P_{(r,l)} = \frac{r^3}{6\, l^3} \tag{1}$$

in which $r = \sqrt{(2A\, E_{r,\min})}$ and $l = 32.7\, E_\gamma/n$, A is the mass of the recoiling atom

---

(9) P. A. SELLERS and P. A. STRAIN, *J. Inorg. Nucl. Chem.* **11**, 84 (1959); L. LINDNER and G. HARBOTTLE, *Ibid.* **15**, 386 (1960).

(10) I. G. CAMPBELL, Polish Academy of Sciences, Institute of Nuclear Research, Report No. 9/V Jan. 1958; *Nukleonika*, **2**, 605 (1957).

E_γ is the total gamma energy following neutron capture (7.92 MeV for ^{32}P), n is the average number of γ-quanta simultaneously emitted – and is set equal to three. $E_{r\,\min}$ is the minimum recoil energy of the recoiling atom required to effect bond rupture. This recoil energy is larger than the bond dissociation energy E_B of the bond to be broken, because part of the energy is lost as kinetic energy of the whole molecule.(11) Consideration of conservation of momentum require that

$$E_{r\,\min} = E_B(A + R)/R \qquad (2)$$

By Equations (1) and (2), inserting the values $E_B = 2.83$ eV (or 65.3 kcal/mole), the mean P–CH$_3$ bond dissociation energy(12) and $R = 45$ (three methyl groups) a value of $E_{r\,\min} = 4.84$ eV is obtained for the minimal recoil energy and therefore $P_{r,t} = 0.14$ per cent for the yield of primary retention in thermal neutron capture in trimethylphosphine. This calculated value is of the same order of magnitude as the observed retention, 0.05 per cent (see Table 3, Run 29).

For thermal neutron capture in phosphine, using the mean bond dissociation energy $\bar{D}$ (P—H) = 3.34 eV, the failure of bond breakage calculated by Equations (1) and (2) is 3.2 per cent. However, the observed yield of ^{32}P-phosphine from a phosphine methane mixture (Run 27) is much larger, and is thus probably due mainly to hydrogen abstraction reactions.

It is of interest to find out to what extent the assumptions inherent in Equations (1) and (2) cause the discrepancy between the calculated and the observed results. It was assumed that three equal quanta of γ-rays were emitted in random direction in space within a time that is short relative to the period of bond vibration, which for the P—C stretching vibration frequency of 652 cm^{-1} in trimethylphosphine(13) corresponds to a time of 5×10^{-11} sec. However the γ-spectrum radiated after neutron capture in phosphorus consists of a number of unequal peaks(14) between which a definite angular correlation has been observed.(15) The resolving time of the coincidence spectrometers for these angular correlation measurements was 2×10^{-8} sec, and it is therefore unknown if one may safely assume three γ-quanta to be emitted within less than 10^{-14} sec.

EXPERIMENTAL

Materials

Trimethyl-, dimethyl-, methylphosphine and phosphine were prepared and purified as described.(1)

1-Butene (Matheson Co.) was used without purification.

Trimethylamine (Fluka AG) was shown by gas chromatography to contain 20 per cent of dimethylamine. The unseparated mixture was used in the scavenger experiments.

Methylphosphinic acid was obtained as described.(1)

Methane was condensed by placing the quartz irradiation tube into a Dewar flask with liquid air, which was cooled by pumping with a mechanical pump to 50 mm. The vapour-pressure of the methane was thus decreased to 5 mm (−198°), and the quartz tube could be sealed without carbonization (which occurred at higher pressures of methane.)

---

(11) H. SUESS, *Z. Phys. Chem.*, **45** B, 297 (1940).

(12) T. L. COTTRELL, *The Strengths of Chemical Bonds* (2nd Ed.) Butterworth, London (1958).

(13) M. HALMANN, *Spectrochimica Acta* **16**, 407 (1960).

(14) L. V. GROSHEV, A. M. DEMIDOV, V. N. LUTSENKO and V. I. PELEKHOV, *Atlas of Gamma Spectra from Radioactive Capture of Thermal Neutrons*. Pergamon, London (1959).
G. A. BARTHOLOMEW and L. A. HIGGS, '*Compilation of Thermal Neutron Capture Gamma Rays*.' Atomic Energy of Canada Ltd. Chalk River Project CRGP 784, AECCL No. 669, 1958.

(15) G. MANNING and G. A. BARTHOLOMEW, *Phys. Rev.* **115**, 401 (1959).

Irradiations

All irradiations were carried out at the innermost position in the thermal column of the Israel Research Reactor No. 1 at a neutron flux of 2 × 10^{10} neutrons $cm^{-2}sec^{-1}$, and a cadmium ratio of 500. The normal reactor temperature is 25°. Trimethylphosphine was irradiated in 40 ml quartz tubes with breakseals, as described.(1) Each tube was accompanied by a small polyethylene tube containing about 40 mg of triphenylphosphine (British Drug Houses) which was counted afterwards and served as a monitor for the total neutron dose absorbed by the trimethylphosphine.

Irradiations at −78° were made for 3 hr by placing the quartz tubes (8 ml volume) into powdered dry-ice in a block of foamed polystyrene in a polyethylene flask.

Separation methods

Gas chromatographic separation of phosphines was carried out using 25 per cent Dow Corning 702 Silicone Fluid on 35–50 mesh firebrick at 50 ± 1° with a 31 ± 1 ml/min flow of helium carrier gas, using a Gow-Mac Model 9193 (TEII) thermal conductivity cell detector at room temperature. Peak maxima appeared at the following times, PH_3, 1.3 ± 0.1 min, $MePH_2$, 2.6 ± 0.2 min, Me_2PH 6.9 ± 0.6 min, Me_3P, 10 ± 1 min.

After distilling out the volatile phosphines in a vacuum system(1) the quartz tube was rinsed out with distilled water (1 or 2 ml) into a volumetric flask. Aliquots (0.025 or 0.05 ml) were used for each chromatography or electrophoresis. Paper chromatography and electrophoresis(2) techniques have been described.

Paper strips after chromatography or electrophoresis were dried in warm air and cut into 1 cm segments which were placed on aluminium plates, covered with Cellotape and counted with Mylar end-window proportional counters under conditions of about 50 per cent geometry.

Acknowledgement—The authors are indebted to Prof. A. HALEVI for stimulating discussions and to the staff of the Israel Research Reactor for carrying out the pile irradiation. This work was supported in part by grant RG-5842 from the U.S. Public Health Service.

J Inorg Nucl Chem, 1963, Vol 25 pp 1351 to 1357 Pergamon Press Ltd Printed in Northern Ireland

RELATION BETWEEN THE PARTITION COEFFICIENT OF GeX_4 MOLECULES (X = Cl, Br, I) AND THE SOLUBILITY PARAMETER OF THE SOLVENT

S Siekierski and R Olszer
Department of Radiochemistry, Institute of Nuclear Research, Warsaw

(*Received* 7 *March* 1963)

Abstract—The extraction of germanium from HCl, HBr and HI acids solutions into 18 inert solvents has been studied The determined distribution ratio has been correlated with the solubility parameter of the extracted GeX_4 molecule and with the solubility parameter of the inert solvent

A PREVIOUS study⁽¹⁾ of the influence of diluent on the extraction of Eu and Th from nitrate solutions by tri-n-butylphosphate has shown that the logarithm of the activity coefficient of the complex ($Eu(NO_3)_3$ 3TBP or $Th(NO_3)_4$ 2TBP) in the organic phase decreases approximately linearly with the increase in the solubility parameter δ_0 of the diluent used From HILDEBRAND'S⁽²⁾ theory of mixtures the following relationship can be derived between the activity coefficient of the complex f_c and the solubility parameter of the diluent δ_0

$$\ln f_c = 1(\delta_0 - \delta_c)^2 \qquad (1)$$

where δ_c denotes the solubility parameter of the extracted complex The author was not able to confirm quantitatively the above relation for the extraction of europium and thorium with TBP for two reasons

(1) The activity coefficient of the complex was calculated from the measured distribution ratio and from the activity of TBP, and was therefore subject to a considerable error

(2) The solubility parameters of the complexes of Eu and Th with TBP are probably much higher than the solubility parameters of the diluents used, and therefore only the far left-hand part of the theoretically predicted parabola could be observed This part might not differ very much from a straight line

The relationship observed has nevertheless shown that the interaction between the complex and the diluent can be explained much better in terms of the solubility parameter of the inert solvent (diluent) than in terms of other physico-chemical constants (dipole moment, polarizability, or dielectric constant) as suggested by other authors One might therefore expect the concept of the solubility parameter to be of general use for the prediction and interpretation of the extraction of inorganic compounds, as has been shown for the extraction of organic compounds ⁽³⁾

To study quantitatively the role of the solubility parameter of the inert solvent (called "diluent" in the previous paper) a simpler case of extraction, viz that of GeX_4, where X = Cl, Br or I was chosen This system has the following advantages compared with that studied previously

---

(1) S SIEKIERSKI, *J Inorg Nucl Chem* **24**, 205 (1962)

(2) J H HILDEBRAND, R L SCOTT, *The Solubility of Nonelectrolytes* Reinhold, New York (1950)

(3) H BUCHOWSKI, *Nature, Lond* **194**, 674-675 (1962)

1 Since the solubility parameter of $GeCl_4$ is low ($\delta_{GeCl_4} = 8.1$) it is possible to use solvents of higher solubility parameter than the parameter of the extracted compound.

2 The influence of the solubility parameter of the extracted compound can be studied with $GeCl_4$, $GeBr_4$ and GeI_4 without a significant change in the structure and properties of the complex.

3 $GeCl_4$, $GeBr_4$ and GeI_4 are extracted by the so called inert solvents (called diluents in the previous paper) and, as a consequence, there should be a direct relation between the extraction coefficient and the solubility parameter of the solvent.

To derive quantitative relations between the extraction coefficient of germanium from hydrochloric hydrobromic and hydroiodic acid solutions and the solubility parameter of the solvent one must assume that the extracted species are $GeCl_4$, $GeBr_4$ and GeI_4. This seems obvious since the extraction of the alternative species H_2GeCl_6 can be entirely excluded in the case of solvents which do not contain donor atoms, and the extraction of hydrated $GeCl_4$ also seems highly improbable, because of the low solubility of water in the solvents used. Macroscale extraction experiments have shown that the ratio of Cl to Ge is four for benzene. But the best evidence for this assumption is the agreement obtained between the theory and experiment. With this assumption, the activity of GeX_4 in the organic phase is related to the solubility parameter of the solvent (δ_0) by the following Equation (2)

$$RT \ln a_{c,o} = V_c \varphi_o^2(\delta_c - \delta_o)^2 - T\Delta\bar{S}_{c,o}^M \tag{2}$$

An analogous equation might be applied to the aqueous phase

$$RT \ln a_{c,aq} = V_c \varphi_{aq}^2(\delta_c - \delta_{aq})^2 - T\Delta\bar{S}_{c,aq}^M \tag{3}$$

where a — thermodynamic activity, V_c — molar volume of GeX_4, φ — volume fraction of solvent, or water, $\Delta\bar{S}_c^M$ — partial molar entropy of mixing, c denotes the complex GeX_4, o — organic phase, aq — aqueous phase. It has been assumed that the molar volume and the solubility parameter of GeX_4 are the same in both phases. Because of the small concentration of GeX_4 the terms φ_o^2 and φ_{aq}^2 are nearly equal to unity and can be omitted in Equations (2) and (3).

Putting $\Delta\bar{S}_c^M = -R \ln x_c$, and assuming that equilibrium between phases has been established ($a_{c,o} = a_{c,aq}$) one arrives at

$$RT \ln \frac{x_{c,o}}{x_{c,aq}} = RT \ln k_x = V_c[(\delta_c - \delta_{aq})^2 - (\delta_c - \delta_o)^2] \tag{4}$$

where k_x is the partition coefficient defined as the ratio of molar fractions.

Since for the purpose of the present work only the change in the partition coefficient with the solvent is important, one of the solvents can be chosen as a standard. Then

$$\ln \frac{k_x}{k_{x,s}} = \frac{V_c}{RT}[(\delta_c - \delta_s)^2 - (\delta_c - \delta_o)^2] \tag{5}$$

where s stands for standard solvent. The assumption has been made that the composition of the aqueous phase is constant, and that V_c has the same value in all th solvents.

Since the molar volumes of the complex and of the solvent may differ quit appreciably in some cases, it seems more reasonable to put $\Delta S_c^M = -R[\ln \varphi_c + (1 - V_c/V)]$ into Equations (2) and (3) instead of the ideal value. φ_c in this expression is the volume fraction of the complex, φ and V are the volume fraction and the molar volume of the solvent, or of the water. Thus, one arrives at the following equation for the ratio of partition coefficients for two solvents, where one has been chosen as a standard

$$\ln \frac{k_\varphi}{k_{\varphi,s}} = \frac{V_c}{RT}[(\delta_c - \delta_s)^2 - (\delta_c - \delta_0)^2] + V_c\left(\frac{1}{V_0} - \frac{1}{V_s}\right) \tag{6}$$

where $k_\varphi = \varphi_{c,o}/\varphi_{c,aq}$ is the partition coefficient defined as the ratio of volume fractions.

Assuming that there is no dissociation or association in the organic phase the ratio of partition coefficients is equal to the ratio of the experimentally measured distribution coefficients $\ln k_x/k_{x,s} = \ln D_x/D_{x,s}$ and $\ln k_\varphi/k_{\varphi,s} = \ln D_\varphi/D_{\varphi,s}$.

It follows from Equation (5) that $\ln D_x/D_{x,s}$ should be a parabolic function of δ_0. The relation between $\ln D_\varphi/D_{\varphi,s}$ and δ_0 is more complicated. The purpose of the present paper was to examine the predictions of the theory in the case of extraction of $GeCl_4$, $GeBr_4$ and GeI_4.

EXPERIMENTAL

Reagents

The solvents used are tabulated in Table 1. They were purified by standard methods. To obtain ^{77}Ge tracer, high purity germanium metal was irradiated in the Polish reactor EWA. The irradiated sample was dissolved in 2 M sodium hydroxide containing H_2O_2. After dissolution concentrated HCl was added to reach a final concentration of HCl about 7.3 M.

Determination of the distribution ratio

To measure the distribution ratio 15 ml of 7.30 M HCl, containing the ^{77}Ge tracer were equilibrated with 15 ml of the solvent for 10 min. The phases were separated, the aqueous phase discarded, and the organic phase equilibrated with a fresh portion of 7.30 HCl without ^{77}Ge trader. This procedure was repeated four times. The aim was to remove ^{77}As, a daughter isotope of ^{77}Ge. As(V) is not extracted from HCl and HBr solutions by inert solvents. The oxidation was accomplished with H_2O_2 during dissolution of the germanium metal. The measured distribution ratios were the same for the second, third and fourth equilibration, which meant that ^{77}As was completely removed in the first equilibration. The result of the fourth equilibration was accepted as the value of the distribution ratio of ^{77}Ge. In the case of extraction from hydrobromic and hydroiodic acid solutions the first equilibration was carried out from HCl solution. Since the distribution ratio of germanium is strongly dependent on the concentration of the acid all the equilibrations were carried out from the same stock solution of HX. All experiments were carried out at 20°C ± 2.

For each diluent at least three independent measurements were carried out. The error of the mean value of the distribution ratio was calculated to be about ± 6 per cent at 95 per cent confidence level.

RESULTS AND DISCUSSION

First, the influence of the germanium carrier concentration on the distribution ratio was investigated. No change in the distribution ratio was found for germanium concentrations ranging from 10^{-4} to 10^{-1} M. All the experiments described below were carried out at a germanium-carrier concentration of 10^{-4} M.

The results of the extraction of germanium from 7.30 M HCl, 6.50 M HBr and 5.20 M HI are shown in Table 1 and Fig. 1. As a standard solvent, hexane has been chosen. Most of the values of the solubility parameters of the solvents were taken from reference (2), those marked by asterisks were calculated from boiling points

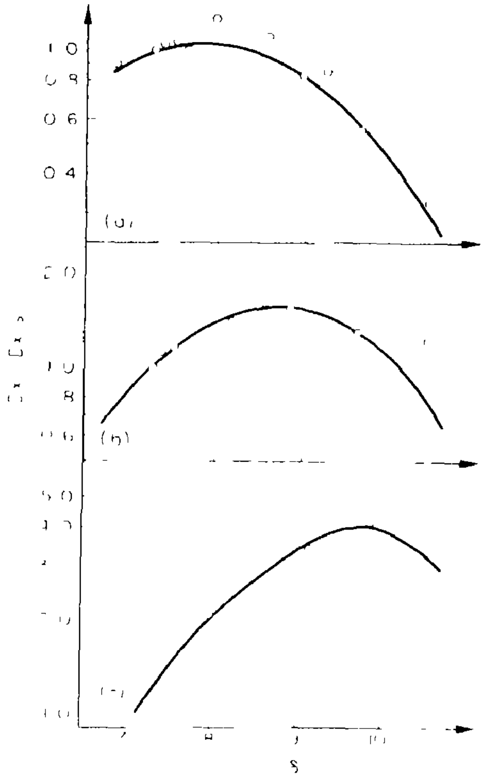


FIG. 1. The dependence of $D_X/D_{X,s}$ on the solubility parameter of the inert solvent. Hexane was used as a standard solvent.
(a) 7.30 M HCl, (b) 6.50 M HBr, (c) 5.20 M HI.

It can be seen from Fig. 1, that there is a qualitative agreement between the experimental data and the theoretical predictions, since the experimental points fit in each case to a parabola predicted by Equation (5). The position of the maximum of the parabola moves from lower to higher values of δ_0, when Cl atoms in GeX_4 molecule are replaced by Br and I atoms. This change is also in accordance with Equation (5), since the following relation between solubility parameters of various GeX_4 molecules is to be expected

$$\delta_{GeCl_4} < \delta_{GeBr_4} < \delta_{GeI_4}$$

To check the agreement between experiment and theory in a more quantitative way two methods were applied.

(1) The values of the solubility parameters of $GeCl_4$ and $GeBr_4$ in each solvent were calculated from Equations (5) and (6) using hexane as a standard solvent and putting $V_{GeCl_4} = 115$ and $V_{GeBr_4} = 125$ (the value for V_{GeBr_4} is that for the solid $GeBr_4$). The value of the solubility parameter should be the same in each solvent. In most cases the values of δ_i calculated for various solvents do not differ very much (Table 1). The differences observed are of the same order as those encountered in the determination of solubility parameters of I_2, SnI_4, S_8 and P_4 from the solubility data.(2) The mean value of δ_{GeCl_4} is very near to that evaluated from the heat of vaporization. The two sets of data, one calculated by means of Equation (5), and

TABLE I

	δ_0	Distribution ratio D_φ			δ_{GeCl_4}		δ_{GeBr_4}	
					Calc from Equation		Calc from Equation	
		GeCl$_4$	GeBr$_4$	GeI$_4$	(5)	(6)	(5)	(6)
Isooctane	6.85	3.16	0.94	—	7.8	8.1	8.4	8.6
n-Hexane	7.3	4.44	1.53	0.76	—	—	—	—
n-Heptane	7.45	4.22	1.55	—	7.9	7.8	8.8	8.8
n-Octane	7.55	3.76	1.40	0.79	7.9	7.5	8.8	8.6
n-Decane	7.7	2.98	1.38	—	7.5	7.3	9.2	8.9
n-Hexadecane	8.0	2.48	1.06	0.71	8.4	7.4	9.1	8.4
Cyclohexane	8.2	5.14	2.52	2.28	7.7	7.7	8.7	8.6
Carbontetrachloride	8.6	6.76	3.27	—	8.1	8.1	8.8	8.8
Toluene	8.90	4.35	2.83	—	7.8	7.8	8.8	8.7
o-Xylene	9.00	3.97	3.15	—	7.9	7.9	9.0	9.0
1,2-Dichloroethylene	9.1	5.63	3.35	—	7.8	7.7	8.6	8.4
Benzene	9.15	4.02	2.99	3.82	7.6	7.6	8.6	8.8
Chloroform	9.3	6.17	3.07	—	8.1	8.0	8.6	8.5
Trichloroethylene	9.3	5.50	3.03	—	8.1	8.1	8.7	8.6
Chlorobenzene	9.5	3.34	2.87	2.83	7.8	7.8	8.8	8.8
1,1,2,2-Tetrachloroethane	9.7	2.67	2.15	—	7.9	7.9	8.7	8.7
1,2-Dichloroethane	9.8	2.71	1.80	—	7.6	7.5	8.3	8.2
Bromoform	10.5	2.13	2.70	5.00	8.0	8.0	9.0	9.0
				Mean	7.87	7.77	8.75	8.76

the other by means of Equation (6) do not differ in the constancy of the δ_c value. This implies that both methods for calculating the partial molar entropy of mixing can be used equally well for evaluating solubility parameters from extraction data.

(2) The other method for comparing the experimental results with the theory is as follows. Equation 5 was rearranged as follows

$$\frac{2.3RT}{\delta_0 - \delta_s} \log \frac{k_r}{k_{r,s}} = -V_c(\delta_0 + \delta_s) + 2V_c\delta_c \qquad (7)$$

The left hand side of the new equation was plotted against $(\delta_0 + \delta_s)$ and a straight line was drawn through the points by the method of least squares (Fig. 2). Again hexane was used as a standard solvent. From the slope of this line and from the intersection with the ordinate, the values of V_c and δ_c were obtained. The results of this calculation are given in Table 2. The agreement with the δ_c and V_c values for GeCl$_4$ determined in other ways is satisfactory, the values of δ_c and V_c for GeBr$_4$ and GeI$_4$ seem to be reasonable. The values of V_c and δ_c obtained by this method were used for the calculation of the parabolas in Fig. 1.

The results of the present study indicate that with the aid of the solubility parameter, predictions concerning the influence of solvent on the extraction coefficient of GeCl$_4$, GeBr$_4$ and GeI$_4$ can be made. The question arises whether the concept of the solubility parameter can be equally well applied to more complicated systems. The system studied in this work may be regarded as a simple one for two reasons: (a) no organic complexing agent takes part in the extraction, (b) the molecules of GeX_4 are symmetric in contrast to those of the majority of complexes encountered in extraction systems of practical importance. As to the first point, the only complication arises from the fact that in the cases where a complexing (extracting) agent is vitally important for extraction, its interaction with diluent must be taken into

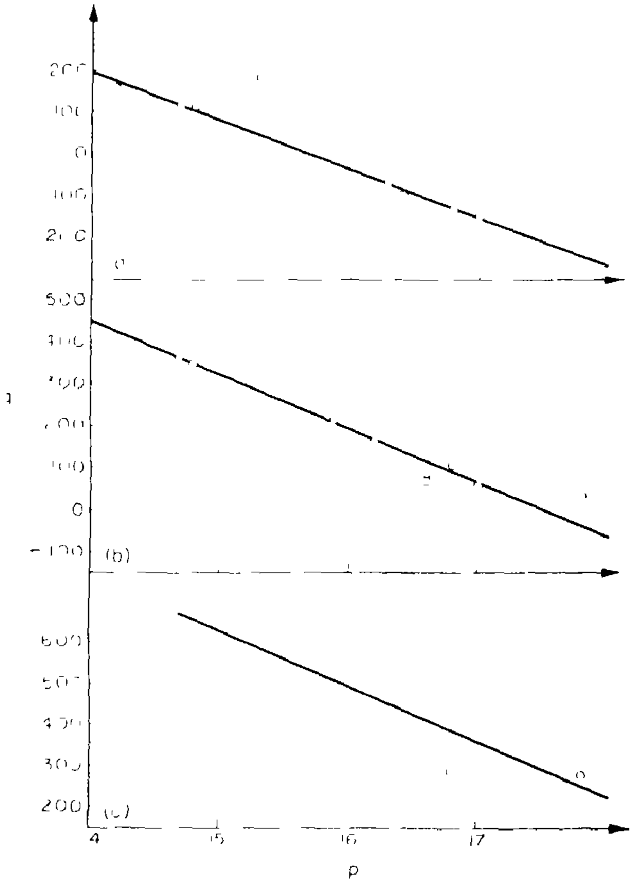


FIG. 2.—The dependence of $q = 2.3\,RT/(\delta_0 - \delta_s)\log k_s/k_{s'}$, on $p = \delta_0 + \delta$.

TABLE 2

GeCl$_4$				GeBr$_4$			GeI$_4$	
δ_t		V_t (cm^3)		δ_t	V_t (cm^3)		δ_t	V_t (cm^3)
From Equation (7)	From the heat of vaporisation$^{(2)}$	From Equation (7)	From Reference (2)	From Equation (7)	From Equation (7)	From molar volume of solid GeBr$_4$	From Equation (7)	From Equation (7)
7.9	8.1	114	115	8.7	131	125	9.8	134

chelate was present, but the amount of water present in the chloroform returned to the blank solubility after the chelate had dissociated.

All of these extraction studies were carried out at 25.0 C. The temperature was quite a critical factor as was already mentioned with respect to the process of centrifuging.

TABLE 2. EFFECT OF CENTRIFUGE-TIME ON THE SOLUBILITY OF WATER IN CHLOROFORM

Sample	Centrifuge time (min)	Temperature	Mg H_2O per 25.00 ml of chloroform
1	1	25.0	36.53
2	1	25.0	34.97
3	1	25.0	35.16
4	1	25.0	34.68
5	1.5	25.0	35.92
6	1.5	25.0	36.51
7	1.5	25.0	36.04
8	1.5	25.0	36.21
9	3	27.5	31.22
10	3	27.5	28.83
11	3	27.5	29.32
12	3	27.5	31.54

It was observed repeatedly that the extraction was 57 per cent complete after a single extraction. Although the literature(1) suggested several methods for improving the per cent extraction, such as multiple stage extractions, increased ligand concentration and varying pH values, it was found that these improvements entailed much greater experimental error rather than less, for the purpose of this experiment.

The per cent extraction (see Table 3) was calculated by making up an aqueous solution of known concentration and measuring the chloroform layer spectrophotometrically. A Beer's Law calculation was applied using the molar absorptivity given in the literature.(1)

TABLE 3.—DETERMINATION OF PER CENT EXTRACTION OF BIS(8-QUINOLINOL) DIOXOURANIUM(VI) SPECTROPHOTOMETRICALLY

Sample	Concentration in aqueous phase originally	Absorbance of Chloroform extract	Concentration found	Per cent Extraction
1	0.0	0.000	0	
2	1.0×10^{-6}	0.142	0.57×10^{-6}	57
3	4.0×10^{-6}	0.605	2.30×10^{-6}	57
4	10.0×10^{-6}	1.450	5.70×10^{-6}	57
			Average	57

The effect of pH in the aqueous phase on the number of molecules of water associated was not investigated as the extraction system had a rather narrow optimum pH range of 8.0–9.0. However, the effect of solubility of water in the chloroform layer as a function of pH was investigated and found to be negligible over the range of pH of the extraction. The results in Table 4 indicate a slight increase in the solubility of water in chloroform with increase of pH in the aqueous layer. However inasmuch as the pH of the experiment was maintained at 8.8 ± 0.1 units, the effect is essentially account. This can be done by determining the thermodynamic activity of the extracting agent in the diluent, as in previous papers.(1 3) As to the second point, the symmetry of GeX_4 molecules does not necessarily imply a drastic difference in interaction with the surrounding molecules, in comparison with the interaction of asymmetric and polar molecules. As a result of the rather high polarity and polarizability of the C X bonds, the interaction of GeX_4 molecules with other molecules includes the same dipole–dipole interaction component as with polar complexes. It seems therefore that the concept of the solubility parameter can be used in the quantitative interpretation and prediction of extraction of other types of complexes, even when they have an appreciable dipole moment and polarizability. This has been shown to be true in a semiquantitative manner in the case of extraction with TBP(1) and long-chain amines.(4)

(4) W. Smulek and S. Siekierski, *J. Inorg. Nucl. Chem.*, **24**, 1651 (1962).

J. Inorg. Nucl. Chem. 1963. Vol. 25, pp. 1359 to 1369. Pergamon Press Ltd. Printed in Northern Ireland

ELECTRONIC STRUCTURE, SPECTRA AND MAGNETIC PROPERTIES OF OXYCATIONS—IV

LIGATION EFFECTS ON THE INFRA-RED SPECTRUM OF THE VANADYL ION

J. SELBIN, L. H. HOLMES, JR.* and S. P. McGLYNN
Coates Chemical Laboratories, Louisiana State University, Baton Rouge, 3, Louisiana

(*Received* 11 *April* 1963)

Abstract—Vanadium–oxygen multiple bond stretching frequencies have been tabulated for fifty-one oxovanadium (IV) and three oxovanadium (V) compounds. The spread of the values may be summarized by $\bar{\nu} = 985 \pm 50$ cm^{-1}, which corresponds to a force constant spread, $k = 7.0 \pm 0.7$ mdyne/Å. The frequency shifts are used to establish several short ligand series, and they are interpreted in terms of σ and π contributions to the vanadium–ligand bond. It is concluded that frequency decreases are directly and primarily caused by decreased $p\pi - d\pi$ donation from oxygen to metal and to increased electrostatic repulsion of the vanadium and oxygen species. The effect may be written

$$\Delta\bar{\nu} = -\sigma(L \to M) - \pi_{\parallel}(L \to M) - \pi_{\perp}(L \to M)$$

where it is estimated that the relative importance of terms is 8 : 2 : 1, and it is assumed that the $M \to L$ donation is negligible for the d^1 vanadium (IV).

IN a continuing study of the spectroscopic properties of metal oxycations,(1,2) we have been investigating the oxovanadium (IV) (vanadyl) ion.(3,4) Experimental evidence for the existence of the vanadyl ion, VO^{2+}, in aqueous solutions is strong, but not unambiguous.(5–8) However, FELTHAM(9) found that the vanadium (IV) ion in aqueous solutions has visible and electron spin resonance spectra which are very similar to those of the solid five-co-ordinated vanadyl complexes and quite different from those of the more symmetric VCl_4 and six-co-ordinated chelates. He concluded that the species present in aqueous solutions is $VO^{2+} \cdot nH_2O$. Further support for the oxycation species in preference to a more symmetrical species such as $V(OH)_2^{2+}$ is summarized by BALLHAUSEN and GRAY.(8) Again the experimental quantity evaluated is the paramagnetic resonance g value.

X-ray diffraction studies of the solid compounds $VOSO_4 \cdot 5H_2O$(10) and $VO(acac)_2$(11) clearly demonstrate the existence and stability of the VO^{2+} entity in solid complexes. This is not surprising when it is realized that even in VO_2, which crystallizes in a highly distorted rutile structure, there is one short V—O bond in each VO_6 unit [12] Chemical analysis and molecular weight determination have also established that the formula of the acetylacetonate (acac) complex is $VO(acac)_2$ and that it is monomeric in benzene [13]

---

* Present address: Southeastern Louisiana College, Hammond, Louisiana.

(1) S. P. McGLYNN, J. K. SMITH and W. C. NEELY, *J. Chem. Phys.* **35**, 105 (1961).

(2) B. SHAMBURGER, M.S. Thesis, Louisiana State University (1960).

(3) J. SELBIN, S. P. McGLYNN, J. K. SMITH, G. A. SIBILLE and L. J. TRUEX, Paper presented at the 16th Southwest Regional ACS-Meeting, Oklahoma City, Okla., Dec. (1960).

(4) J. SELBIN, L. H. HOLMES, JR. and S. P. McGLYNN, *Chem. and Industr.* 746 (1961).

(5) L. P. DUCRET, Thesis, Paris University (1951).

(6) F. J. C. ROSSOTTI and H. S. ROSSOTTI, *Acta Chem. Scand.* **9**, 1177 (1955).

(7) C. K. JORGENSEN, *Acta Chem. Scand.* **11**, 73 (1957).

(8) C. J. BALLHAUSEN and H. B. GRAY, *Inorg. Chem.* **1**, 111 (1962).

(9) R. D. FELTHAM, Thesis, University of California, UCRL-3867 (1957).

(10) M. B. PALMA-VITTORELLI, M. U. PALMA and F. SGARLATA, *Nuovo Cimento* (Series 10) **3**, 718 (1956); G. LUNDGREN, *Rec. Trav. Chim.* **75**, 585 (1956).

(11) R. P. DODGE, D. H. TEMPLETON and A. ZALKIN, *J. Chem. Phys.*, **35**, 55 (1961).

Indirect evidence for the mononuclear monoxy VO^{2+} species may be deduced from the infra-red spectra of vanadyl compounds BARRACLOUGH *et al* [14] examined the infra-red spectra of several complex metal compounds which were presumed to contain metal oxygen multiple bonds They reported that the stretching frequencies of metal-oxygen double bonds may generally be found between 900 and 1100 cm^{-1} Specifically they reported probable V—O stretching vibrations for the following four compounds $VOSO_4$, 987, 1003, 1020, $VO(acac)_2$ 995, $(NH_4)_2[VO(ox)_2]\,2H_2O$, 976, and $(NH_4)_2[VO(mal)_2]\,4H_2O$, 967, 977 (see footnote to Table 1 for abbreviations used) Earlier vanadium (IV) hydroxide had been formulated as $VO(OH)_2$ on the basis of its infra-red spectrum [15] which shows a strong band at 955 cm^{-1}, attributed to the V—O stretching vibration

It is apparent from the above values for band maxima that the environment of the VO^{2+} entity conditions a marked effect upon the stretching frequency, and hence upon the force constant and strength of the V—O bond This is not unexpected and, in fact, McGLYNN and co-workers[1] have shown that the infra-red bands due to the dioxouranium (VI) symmetric and antisymmetric stretching vibrations may be used as a probe to establish a ligand series exhibiting a striking parallelism with the spectrochemical series

The persistence of the oxovanadium (IV) species in a number of compounds makes possible the utilization of the properties of the oxycation species in a study of the bonding structure of complexes of this d^1 electron system Ideally, one might expect not only to be able to study the symmetry types available to this transition metal ion, but also to learn more about the nature of the bonding to various ligated species as they perturb the VO^{2+} entity Thus the stretching frequency of the metal–oxygen bond should serve as a sensitive probe from which certain structural and bonding features may be deduced Furthermore, the oxymetal species will show electronic localized charge-transfer absorption bands (e g , arising from electron transfer from orbitals located primarily on the oxygen to orbitals primarily located on the metal) in addition to those normally observed with d^n ions These additional bands may be expected to be independent upon the other ligands and the strength and symmetry of the ligand field

In this paper we shall be concerned only with the interpretation of the infra-red spectra of vanadyl compounds A subsequent paper[16] will deal in detail with the electronic spectra The electronic energy levels in the vanadyl entity and in its complexes have been deduced from a combined crystal-field and molecular orbital approach and it is determined (see Appendix) that there is no basic disagreement with the molecular orbital scheme of BALLHAUSEN and GRAY [8]

---

[12] B ANDERSON, *Acta Chem Scand* **10,** 623 (1956)

[13] M M JONES *J Amer Chem Soc* **76,** 5995 (1954)

[14] C G BARRACLOUGH, J LEWIS and R S NYHOLM, *J Chem Soc* 3552 (1959)

[15] C CABANNES-OTT, *C R Acad Sci , Paris* **242,** 2825 (1956)

[16] S P McGLYNN, J SELBIN, T R ORTOLAND, G MAUS, and W JORDAN, in preparation for publication.

It appears that the vanadium in the vanadyl may be either five- or six-coordinated [13,17] and it is not always certain which obtains in a given compound. However, chemical analysis coupled with molecular weight and/or conductance data will generally suffice to settle this point.[18]

In sum, we have examined the infra-red spectra of thirty-nine vanadyl complexes, thirty of which are new compounds whose preparation and properties are reported elsewhere.[18] Stretching frequencies of the perturbed VO^{2+} species have been assigned, certain ligand series established and discussed.

EXPERIMENTAL

The new compounds studied in this investigation were prepared and characterized according to procedures previously outlined.[18] Known compounds were prepared according to procedures found in the literature. Starting materials included reagent grade vanadyl sulphate, vanadyl chloride, ammonium metavanadate and vanadium (V) oxide. All other chemicals used were of reagent grade quality or better.

Infrared spectra in the range 5000–650 cm^{-1} were obtained with a Perkin-Elmer Model 21 and a Beckman IR-7 recording spectrophotometer, both employing NaCl optics. Polystyrene film was used to calibrate the instruments. Spectra were run with the samples in Nujol mulls since these gave better spectra than the alkali halide pellet technique. Interaction of some of the compounds with the alkali halide under the conditions necessary for pellet preparation was evident. Spectra of all ligands and/or complexes of other transition metal ions with the ligands were obtained and using these, there was usually no difficulty in assigning the band(s) of the perturbed VO^{2+} stretching vibration. In those cases in which the ligands have bands in the region of the metal–oxygen stretch, comparisons were made with the spectra of analogous complexes of other divalent metal ions of the first transition series.

Infrared spectra of many of the vanadyl complexes studied in this work were run in solution in a concurrent investigation to be reported elsewhere.[19] In all of those cases where solubility was effected in an inert solvent the value for the V–O stretch varied no more that ± 5 cm^{-1} from the value found with the solid complex.

RESULTS AND DISCUSSION

Table 1 lists the frequencies assigned to the vanadium-oxygen multiple bond stretching vibration for fifty-one oxovanadium (IV) and three oxovanadium (V) compounds. In those cases where more than one band was observed in the metal–oxygen multiple bond stretch region, the strongest is listed first. The values enclosed by parentheses were taken from the literature cited.

The force constants, k, have been related to the frequency using a simple harmonic expression, and are found to vary from 7.68 for $VOCl_3$ to 6.23 for $[VO(DMSO)_5](ClO_4)_2$ in mdyne/Å. The listing in Table 1 may then be approximately summarized by the single values $k = 7.0 \pm 0.7$ and $\bar{\nu} = 985 \pm 50$ cm^{-1}, it behoves the authors to illustrate then that the spread of the effect being observed is larger than that which could arise from (a) lattice forces or (b) simple mechanical coupling to the metal-ligand vibrations.

(a) Certainly, some of the shift observed to occur in the V—O stretch frequency can undoubtedly be caused by the operation of lattice forces which are expected to vary from one solid compound to the next. However, the magnitude of the crystalline-environment effect is considered to be small. Specifically, some of the compounds

---

[17] R. T. Claunch, T. W. Martin and M. M. Jones, *J. Amer. Chem. Soc.* **83**, 1073 (1961).

[18] J. Selbin and L. H. Holmes, Jr., *J. Inorg. Nucl. Chem.* **24**, 1111 (1962).

[19] J. Selbin, H. R. Manning and G. Cessac presented at the 17th Southwest Regional A.C.S. Meeting, Dallas, Texas, December 1962, *J. Inorg. Nucl. Chem.* In Press.

TABLE 1 —VANADIUM-OXYGEN STRETCHING FREQUENCIES, OXOVANADIUM (IV) AND (V) COMPOUNDS

	Compound*	V—O stretch, cm^{-1}
1	$VOCl_3$	(1035)(24)
2	$VOBr_3$	(1025)(21)
3	V_2O_5	1020 (1020)(14)
4	[VO(*p*-OCH_3-TPP)]	(1015)(22)
5	$VOSO_4$ $5H_2O$	*1003*, 1017, 975 (1020, 1003, 987)(11) (1008)[9], (980)(23)
6	[VO(phthal)]	1003
7	[VO(*p*-Cl-TPP)]	(1002)(22)
8	[VO(TPP)]	(1001)(22)
9	[VO(*p*-CH_3-TPP)]	(1001)(22)
10	$[VO(Benzac)_2]$	(1001)(9)
11	$[VO(DBM)_2]$	(1000)(9)
12	$[VO(sal)_2]$	(998)(9)
13	$(Et_4N)_3[VO(NCS)_5]$	*997*, 979*m*
14	$[VO(acac)_2]$	996 (995)(22), (1005)[10], (995)[21], (1000)(24)
15.	$VOBr_2$ H_2O	996
16.	[VO(Etiopor)]	(995)(25)
17	$VO(ClO_4)_2$ xH_2O	995
18.	$(NH_4)_2(VO)_2(SO_4)_2$	991 *br*
19	$VOCl_2$ xH_2O	990
20	[VO(ophen) (ox)]	*989*, 959*m*
21	$(Me_4N)_3[VO(NCS)_5]$	*987*, 979
22	$[VO(ophen)_2](ClO_4)_2$	987
23	VOF_2 xH_2O	984
24	$(Me_4N)_2[VOCl_4(EtOH)]$	*982*, 969, 958*sh*
25	$K_3[VO(NCS)_5]$	*982*, 969*sh*
26	$[VO(ophen)_2Cl]Cl$	*982*, 960*sh*, 908*w*
27	$[VO(ophen)_2Br]Br$ H_2O	*981*, 984*sh*, 908*w*
28	[VO(en-bis-sal)]	990, (980)(26), (990)(9)
29	$[VO(oxine)_2]$	979
30	$[VO(dipy)SO_4]$	979
31	[VO(dipy) (ox)]	979
32	$[VO(dipy)_2](ClO_4)_2$	*979*, 923*m*
33	$[VO(ophen)SO_4]$	978
34	$VO(dipy)_{1.5}(NCS)_2$	*977* 967
35	$(NH_4)_2VO(mal)_2$ $4H_2O$	(*977*, 967)(11)
36	$(NH_4)_2VO(ox)_2$ $2H_2O$	(976)(14)
37	$VO(ophen)_{1.5}(NCS)_2$	*973*, 963*sh*
38	VO(ox) H_2ox $3H_2O$	*973*, 988*sh*
39	$Na_2VO(edta)$ $5H_2O$	(970)(27)
40	$[VO(ophen)F_2]$	*968*, 964, 928*m*
41.	$[VO(dipy)F_2]$	*968*, 957, 949*sh* 932*w*
42	$VO(OH)_2$	*968*, 962 (955)(16)
43	$[VO(dipy)_2Cl]Cl$	*965*, 973*sh*
44	$[VO(acac)_2py]$	(964)(23)
45	$VO(ophen)_2SO_4$	*960*, 923*sh* 911, 900

Table 1 (cont)

	Compound	V—O stretch, cm^{-1}
46	$[VO(dipy)_2Br]Br\ N_2O$	*958*, 972*sh*
47	$(Et_4N)_3[VO(CN)_5]$	*956*, 965*sh*
48	$[VO(DMSO)_3SO_4]$	*954*, 964*sh*
49	$Cs_3[VO(CN)_5]$	*953*, 968*sh*
50	$(Me_4N)_3[VO(CN)_5]$	952
51	$[VO(DMSO)_5]Br_2$	950br, *sh*
52	$[VO(DMSO)_3Cl_2]$	*948*, 962*sh*, 936*sh*
53	$(NH_4)_3[VOF_5]$	*947*, 937
54	$[VO(DMSO)_5](ClO_4)_2$	*932*, 955, 962*sh*

* ABBREVIATIONS TPP tetraphenylporphine, phthal phthalocyanine, Benzac = benzoylacetonate ion, DBM dibenzoylmethanate ion, sal - salicylaldehyde, Et - ethyl, acac acetylacetonate ion, Etiopor - etioporphyrin I, ophen = orthophenanthroline, ox = oxalate ion, Me = methyl, en-bis-sal = ethylenediamine-bis-salicylaldehyde, oxine oxinate ion, mal malonate, edta ethylenediaminetetraacetate ion, DMSO = dimethylsulphoxide, *sh* = shoulder, *m* medium, *w* - weak, *br* broad

All bands not otherwise marked are strong or very strong in their respective spectrum The values listed for compounds 4, 7, 8 9, 28 and 39 were taken from the literature cited, although the authors did not assign the values to the V—O stretch

listed in Table 1 are soluble in inert solvents and the V—O stretch found for the solubilized complex varied no more than ±5 cm^{-1} from the value found with the solid complex

(b) It is probably quite correct to assume that coupling of the V—O stretch with vanadium–ligand modes is insignificant for ligand masses which exceed, individually, 40 a m u This assertion becomes tolerable even for ligands of low mass if the vanadium–ligand vibrational modes are of low frequency, as they are generally believed to be Nonetheless, this effect could become significant in certain cases, and cannot be dismissed too lightly Our experience, here as elsewhere, suggests to us that such coupling is relatively unimportant, and this assumption is inherent in our future discussion

The effect of individual ligand to metal bonds on the V—O stretching mode is considered below It is presumed that the appendix will be consulted for further detail

σ-Bonding The vanadium-oxygen bond in vanadyl compounds is a multiple covalent bond consisting of $p\pi \rightarrow d\pi$ donation of electrons by the oxygen to the vanadium superimposed upon the σ-bond (see appendix) The amount (or degree) of $p\pi \rightarrow d\pi$ donation depends both upon the tendency of oxygen to donate and

---

(20) H J EICHHOFF and F WEIGEL, *Z Anorg Chem* **275,** 267 (1954), F A MILLER and L R COUSINS, *J Chem Phys* **26,** 329 (1957)

(21) F A MILLER and W K BAER *Spectrochim Acta* **17,** 112 (1961)

(22) K UENO and A E MARTELL, *J Phys Chem* **60,** 934 (1956)

(23) K NAKAMOTO, Y MORIMOTO and A E MARTELL, *J Amer Chem Soc* **83,** 4533 (1961)

(24) K E LAWSON, *Spectrochim Acta* **17,** 248 (1961)

(25) J G ERDMAN, V G RAMSEY, N W KALENDA and W E HANSON *J Amer Chem Soc* **78,** 5844 (1956)

(26) K UENO and A E MARTELL, *J Phys Chem* **60,** 1270 (1956)

(27) D T SAWYER and J M MCKINNIE, *J Amer Chem Soc* **82,** 4191 (1960)

vanadium to accept electrons The donating tendency of the oxygen, which may be associated with the high electron density in the filled valence level of the small oxygen atom,(28) should be very little affected by the presence of co-ordinated ligands However, the electron-accepting capacity of the vanadium (IV), which has four empty d-orbitals and one half-filled d-orbital, should be markedly affected by co-ordinated ligands Thus, co-ordination to ligands which owe their ligational strength primarily to their σ-electron pair (Lewis Base) donating ability, will increase the electron density in the metal atom d-orbitals and effect a reduction in the amount of $p\pi \rightarrow d\pi$ donation from the multiply bonded oxygen This lowering of the V—O bond order should be reflected in a lowering of the vanadium–oxygen stretching frequency The greater the donation of ligand electrons to the vanadium, the greater will be the decrease expected in the V—O stretching frequency Both the a_1 and e-orbitals (see appendix) are stabilized in a fashion which increases with increasing σ-donor capacity of the ligand and which indicates a small shift of charge toward the vanadium atom However, the $b_1(L) \rightarrow b_1(M)$ is the most important contribution from a vibrational sense, since, despite no significant effect on the VO bond strength *per se*, it does lead to a considerable piling-up of charge in a b_1-orbital of the metal which was previously unoccupied, and thus by secondary electrostatic repulsion to a destabilization of the V—O bond It is undoubtedly this very effect which is manifested in the decrease of the vanadyl stretch upon going from V(V) compounds such as $VOCl_3$ to V(IV) compounds such as [VO(phthal)] where a net change of 32 cm^{-1} occurs In actuality $VOCl_3$ should be compared with a compound K_2VOCl_4 or K_3VOCl_5 in which a net decrease of some 70 or 80 cm^{-1} might be expected Similarly a decrease(11) of some 90 cm^{-1} is observed upon going from $TiO(acac)_2$ to $VO(acac)_2$, there is some uncertainty associated with the $TiO(acac)_2$ frequency because of possible polymerization of titanyl systems Despite this it seems reasonable to assume that the population of the π-group orbital of the MO^{2+} species which occurs on going from V(V) to V(IV) oxycation species, or from TiO^{2+} to VO^{2+} is the primary reason for the decrease of the M—O stretching frequency It has now been suggested that population of the b_1 component of the original π-orbital occurs in complexes, and to an extent roughly proportional to the σ-donor capacity of the ligand It seems reasonable therefore that the decrease of V—O stretching frequency which occurs in vanadyl complexes is a rough measure of this donor capacity

$\pi_\perp$-bonding Considerations here are exactly the same as those for σ-bonding except that all overlaps are less by a factor of ~8, and the importance of $\pi_\perp(L \rightarrow M)$ donation is accordingly minimized No $M \rightarrow L$ contribution is significant even in unsaturated ligands

$\pi_\parallel$-bonding There is a contribution of charge from the ligand to the original b AO This effect may be expected to amount to some $\frac{1}{3}$ of the σ-effect since the $\int b_2(L)b_2(V)\,d\tau$ overlap (see appendix) is of the order of $\frac{1}{3}$–$\frac{1}{4}$ of the corresponding b overlap, and as such is of importance

In sum it is concluded that the frequency changes are directly related to decreas $p\pi \rightarrow d\pi$ donation from oxygen to metal and to increased electrostatic repulsion the vanadium and oxygen species and that this effect may be written

$$\Delta\tilde{\nu} = -\sigma(L \rightarrow M) - \pi_\parallel(L \rightarrow M) - \pi_\perp(L \rightarrow M)$$

---

(28) R J GILLESPIE, *J Amer Chem Soc* **82**, 5978 (1960)

It is impossible to estimate accurately the relative importance of changes in the bonding between the vanadium and oxygen since the energy calculations yield only the one-electron energies of the total complex, and not of one bond region It is estimated that the terms in the above equation are of relative importance 8 2 1, and that the $M \rightarrow L$ donation is entirely neglectable in complexes of d^1 vanadium (IV) It is further difficult to estimate the effects of the fifth ligand, and the only simple conclusion is that no direct electrostatic effect is expected (see appendix)

We now proceed to discuss the results obtained on the basis of the attitudes presented in the foregoing At least eleven different compound types are discernible among the vanadyl complexes listed in Table 1 They are, with the number of representatives of each type [VOa_5], 10 (only 5 different a's), [$VO(AA)_2a$] 7, [VO(AAAA)], 6, [$VO(AA)_2$], 4, [VO(AA)(BB)], 4, [$VO(AB)_2$], 3, [$VO(AA)a_2$], 2, [VO(ABBA)], [$VO(AA)a_3$], [VOa_1b] and [VOa_3b_2], 1 each In addition there are four compounds of the type VOX_2 xH_2O Among the first type we observe the following order of ligands corresponding to decreasing frequency H_2O NCS^- CN^- DMSO $\sim$ F This order should therefore correspond to increasing electron donation ability from left to right The unexpected extreme position of fluoride may be explained by its strong tendency to delocalize its p-electrons away from its compact filled valence level It has only recently been proposed(28) that multiple bonding by fluoride (and oxide) should be expected when it is bonded to an atom or grouping which can readily accept π-bonding electrons The strong repulsions between the non-bonding electron pairs located on the small fluorine atoms will cause them to be partially delocalized into empty orbitals of a bonded atom In this way the high electron density on the relatively small atom can be relieved It is interesting to note that the fluoro complexes of VO^{2+} have been found(29) to be much more stable in aqueous solution than the chloro complexes Furthermore, the fluoro complexes of VO^{2+} are much stronger than those of the similarly sized Cu^{2+} Zn^{2+} and Ni^{2+} ions all of which have heavily populated d-orbitals The position of dimethylsulphoxide is surprising but perhaps not very much so in view of the large number of very stable complexes it can form with a great many transition and nontransition metals (30) The intermediate position of cyanide compared with its extreme position in the spectrochemical series is perhaps to be traced to the fact that a large portion of its ligational strength derives from its capacity to accept π-bonding electrons originating on the metal ions As already stated, the vanadyl ion would be expected to be a very poor donor metal ion as compared with later transition metal ions having more populated d-levels Finally, the oxygen of the neutral water molecule does not suffer from the high charge density of, for example, that of the oxide ion with the possible exception of NCS , it is surely the poorest Lewis base of the series Both of these factors must contribute to its extreme position

Turning now to the second type of complex [$VO(AA)_2a$], we arrive at the series ophen mal $\sim$ ox dipy The relative positions of the two nitrogen bases are reversed from those found in the spectrochemical series However the spectrochemical series has found to hold generally for the later transition elements which can partake in back-donation π-bonding and in this respect it is not unusual that the more highly conjugated ophen is a "stronger" ligand than dipy However, with vanadyl, where back donation is unimportant, it might be expected that the more flexible (spatially) molecule, would form the stronger bonds It should be pointed out that the same relative positions of these two ligands is observed for the [VO(AA)$_2$] compounds, where the order is DBM > acac ophen dipy Again, with the [VO(AA)(BB)] compounds we find ophen dipy Finally, the same inversion of the normal order is found$^{(1)}$ in UO_2^{2} complexes of ophen and dipy

---

(29) S Ahrland and B Noren *Acta Chem Scand* **12**, 1595 (1958)

(30) J Selbin and L H Holmes Jr, *J Inorg Nucl Chem* **16**, 219 (1961) F A Cotton and R Francis, *J Amer Chem Soc* **82**, 2986 (1960) F A Cotton, R Francis and W D Horrocks, *J Phys Chem* **64**, 1534 (1960)

That the structurally similar and rigidly planar four-nitrogen quadridentate bases (TPP, its para-substituted derivatives and phthalocyanine) all give vanadyl complexes with similar V–O frequencies is expected, as are the rather high values for these frequencies (1001 1015 cm^{-1}) Furthermore, from an electrostatic viewpoint it is not unexpected that the two-oxygen bidentate ligands with a formal minus one charge (benzac, DBM sal, and acac) should lead to higher frequencies (996–1001 cm^{-1}) than those with a formal minus two charge (mal, ox, 976–977)

In conclusion, we might point out that while the V–O stretch frequencies for a large number of complexes have been reported here, the wide variety of complex and symmetry types reduces markedly the number of complexes that can be subjected to meaningful comparison We shall have to wait for the results of studies now in progress to draw more meaningful and extensive conclusions concerning the bonding role of various ligands in oxycation species

Acknowledgments--The authors wish to thank the National Science Foundation (Grant No NSF-15242) and The Research Corporation for financial support

APPENDIX

It will be assumed that all vanadyl complexes are of C_{4v} symmetry This is undoubtedly an incorrect assumption for some, if not all, of the complexes of Table 1, however, the use of this approximation should not affect in any way the rather general conclusions of this section

The vibrational frequencies tabulated in Table 1 are presumed to correspond to V—O stretching vibrations Since the primary effort is to understand the manner in which various ligands influence this frequency, and conversely, to make use of the frequency variation to determine certain characteristics of the ligands, it would seem that a theoretical approach similar to the rather thorough one of BALLHAUSEN and GRAY$^{(8)}$ would require considerable effort but would probably be infertile One must rather consider the vanadyl complex in a stepped fashion

(1) The electronic structure of the V—O^{2+} entity must first be elaborated,

(2) the equatorial ligands must next be coupled to the V—O^{2+} species, and the manner in which such ligands influence the strength of the polar V—O bond delineated, and finally

(3) where appropriate the fifth (polar) ligand must be introduced, and the modifications consequent to such introduction prescribed

This procedure is similar to that previously used in a discussion of uranyl complexes$^{(1)}$ The orbitals used were the $2p$ AO's of the vanadyl oxygen, the $3d$, $4s$, and $4p$ AO's of the vanadium atom and the σ, $\pi_\perp$ and $\pi_\parallel$ GO's of the nearest neighbour equatorial ligand atoms These latter group orbitals are easily visualized by reference to Fig 1, negligible. The ionic strength was maintained at a constant value 1.0×10^{-3} over all of the pH range by addition of sodium perchlorate to the aqueous phase.

The effect of ionic strength in the aqueous phase on the solubility of water in chloroform was deemed negligible through experiments analogous to the pH effect experiments. Solutions of known ionic strength were prepared by dissolving solid sodium perchlorate in de-ionized water. Table 5 shows the results of these experiments.

It was apparent from this data that below an ionic strength of 0.010, there was no effect on the solubility of water in chloroform. At values of ionic strength greater than 0.010 the effect was small below an ionic strength of 1.000.

It was significant that the ionic strength was always somewhat less than 0.010 for the bis(8-quinolinol) dioxouranium(VI) extractions and varied by no more than a factor of ten.

TABLE 4. EFFECT OF pH ON SOLUBILITY OF WATER IN CHLOROFORM

pH	Mg water dissolved per 25.00 ml of chloroform*
11.0	33.92
9.0	34.10
8.0	33.18
7.0	32.92
5.0	31.84
3.0	32.11

* Each value is the average of four titrations.

TABLE 5. – EFFECT OF IONIC STRENGTH ON SOLUBILITY OF WATER IN CHLOROFORM

Ionic strength	Mg of water dissolved per 25.00 ml of chloroform*
0.001	30.63
0.005	31.00
0.010	30.67
0.050	29.62
0.100	29.80
1.000	28.42
5.000	25.40

* Each value is the average of four titrations.

where the axes adopted are also specified, the equatorial group orbitals and their energies are given in Table 2 Only the np-AO's of the fifth (possible) ligand are considered, where n is the highest energy partially filled or filled orbital of the nearest neighbour atom of the fifth polar ligand

The one-electron levels of a VO^{2+} entity are shown on the left of Fig 2 This level diagram is principally qualitative and represents the solution of various secular equations the integrals in which were estimated by methods set out by FELTHAM[9] and by McGLYNN and SMITH[31] In such a species the ground state configuration ($C_{\infty v}$ point group) would be $\pi^4\delta^1$ $^2\Delta$, and the two lowest energy intra-d-shell transitions would be $^2\Delta \rightarrow {}^2\pi$ and $^2\Delta \rightarrow {}^2\Sigma^+$, at 1 5 and 2 3 eV respectively, and of which only the former is weakly allowed In so far as such a consideration is pertinent, the crystal field splitting is given by Δ (or 10 Dq) $\sim$ 2 3 eV, and there is a considerable component of π-bonding in the net-bonding of the V^{4+} and O^{2-} species This latter conclusion, originally shown to be valid for UO_2^{2+} ions[31] has since been further validated by more sophisticated calculation[8] in the case of VO^{2+}

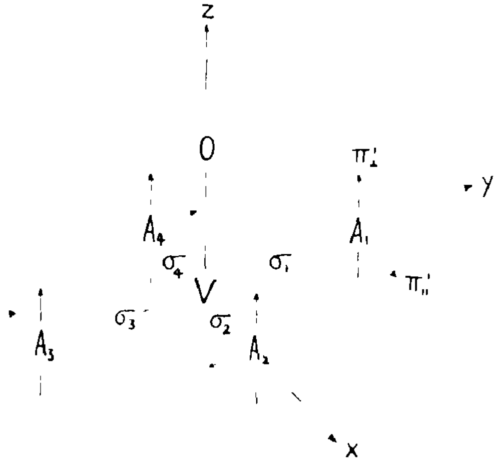


FIG 1 —The z-axis, as also the arrows representing the $\pi_\perp$ AO s are perpendicular to the plane of the paper The A's represent the nearest neighbour atom of the ligand L Point group is C_{4v}

TABLE 2 - EQUATORIAL GROUP ORBITALS SYMMETRIES AND ENERGIES

General orbital	σ*	$\pi_\perp$†	$\pi_\parallel$‡	Energy§
$1/2(\phi^1 + \phi^2 + \phi^3 + \phi^4)$	a_1	a_1	b_2	$\alpha \quad 2\beta_\sigma$
$\frac{1}{\sqrt{2}}(\phi^1 - \phi^3)$, $\frac{1}{\sqrt{2}}(\phi^2 - \phi^4)$	e	e	e	α
$1/2(\phi^1 - \phi^2 + \phi^3 \quad \phi^4)$	b_1	b_1	a_2	$\alpha \quad 2\beta_\sigma$

* $\phi^i \quad \phi^i$

† $\phi^i \quad \pi_\perp{}^i$

‡ $\phi^i = (\quad 1)^{i+1}\pi_\parallel{}^i$

§ β is the resonance integral and is negative, for σ the substitution $\sigma \quad \pi$ and π is to be made where appropriate, the relative order of integrals is , $|\beta_\sigma| \quad |\beta\pi| \quad |\beta\pi|$

---

[31] S P McGLYNN and J K SMITH, *J Mol Spect* 6, 164 (1961)

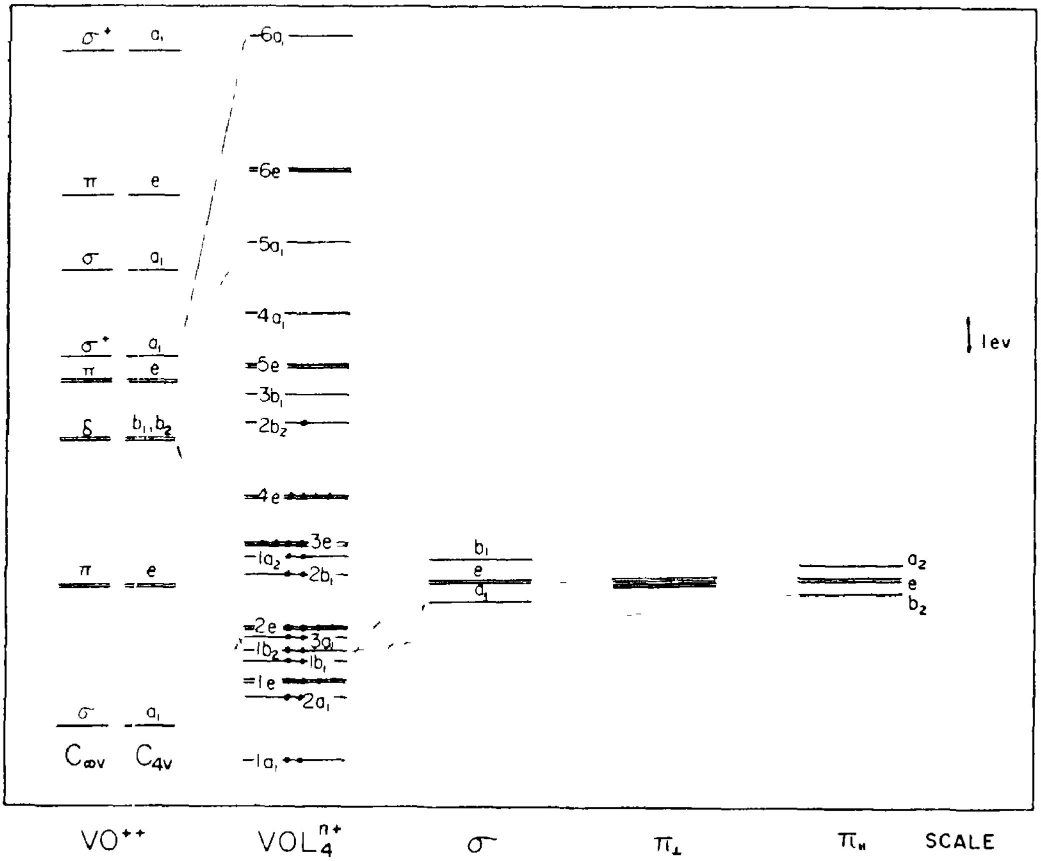


FIG 2 —An energy level diagram of a VO++ species (left), a VOL$_4^{n+}$ species (centre) and a D_{4h} ligand arrangement (right) L signifies a general ligand, and n may be positive or negative This diagram is of a semi-qualitative nature, and corresponds closely to that of BALLHAUSEN and GRAY(8) The energy of the ligand orbitals is naturally variable and dependent on L, the VOL$_4$ levels are also variable but to a lesser extent Only a sufficient number of correlation lines are shown to identify the principal interactions discussed in the text

The equatorial ligand levels are shown schematically on the right of Fig 2, and the composite orbitals are shown in the centre of the same figure It is not intended to go into the details of this calculation, nor to elaborate all the spectral consequences of this particular ordering of energy levels since this will be the object of a further paper(16) on the electronic spectra of the vanadyl complexes considered in the present work However, it is well to point out the following

(a) The $\delta(C_{\infty v})$ level is split into two components, b_2 and b_1 in C_{4v} The b_2 level remains unchanged (increase of 0 1 eV) energetically since it interacts only with the b_2 ligand group orbital of π type, and the overlap is small However, the b_1 orbital overlaps strongly with one of the σ-group orbitals of the ligands, and very weakly with one of the π -group orbitals As a result the b_1 MO is increased in energy by an amount 1 3 → 1 8 eV dependent on the nature of the ligand In other words we conclude that the relative positions of the b_1 and e MO's are determined by the ligands and that the exact order is capable of inversion This is a result which must be borne in mind when interpreting electronic spectra, and which may be considered an adjunct to the conclusions of BALLHAUSEN and GRAY (8)

(b) The ground state of the vanadyl complex is given by b_2, ${}^2B_2$, and there are now three intra-*d*-shell transitions possible ${}^2B_2 \rightarrow {}^2B$, ${}^2B_2 \rightarrow {}^2E$ and ${}^2B_2 \rightarrow {}^2A_1$ The energies of the first two transitions may invert in complexes in which the ligands are strong σ-donor species, while the third transition may overlap significantly with the ${}^2B_2 \rightarrow {}^2A_1(4S)$ transition, and may very well be completely occluded by charge-transfer bands

(c) Insertion of the fifth (polar) ligand would not be expected to have serious consequences for Fig 2 It may lead to slight destabilization or stabilization of the original V–O bond depending on whether it is more or less electronegative than oxygen It will generally tend to raise the energy of the e MO relative to the b_1 MO.

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 1371 to 1374. Pergamon Press Ltd. Printed in Northern Ireland

ELECTRON POLARIZATION AND DIAMAGNETIC SUSCEPTIBILITY

S. K. K. JATKAR, V. S. JATKAR and A. J. MUKHEDKAR
Department of Chemistry, University of Poona, Poona 7, India

(*Received* 13 *November* 1962, *in revised form* 22 *April* 1963)

Abstract—A semi-empirical relation between electron polarization P_E and diamagnetic susceptibility χ_M is derived

$$-\chi_M = P_E \frac{\pi}{2}\frac{r^2}{\lambda_0^2}$$

where r is the effective radius of the atom and λ_0 is the characteristic wavelength. The calculated values of r are of the order of the atomic radii. It is concluded that the dispersion electrons have major contributions to total diamagnetic susceptibility.

A NUMBER of papers have been published on the empirical study of diamagnetism. Most of them are based on the application of the empirical Pascal's constants for atomic diamagnetism and structural diamagnetism.[1] Recently POPLE[2] devised an independent electron molecular orbital theory for diamagnetism; the theory provides a convenient basis for detailed interpretation of the Pascal's constants. VAN VLECK[3] derived a quantum mechanical equation of diamagnetism in terms of wave-functions for the molecule is the absence of a magnetic field; the calculations were well involved and were in good agreement for simple molecules like hydrogen and helium. BHATNAGAR and coworkers[4] empirically derived the relation between diamagnetic susceptibility and the square of the radius of the molecule calculated according to the Bragg's method of closest packing of atoms and found to be satisfactory for electronic isomers. However it approximately holds good only for organic compounds, while it does not hold for isoelectronic inorganic compounds,[5] even containing the same number of atoms. MATSUNAGA and coworkers[6] formulated an empirical relationship between diamagnetic susceptibility and the radius of the π-orbital for a number of polynuclear aromatic compounds. The correlation between electric polarizability and magnetic susceptibility derived, by VINTI[7] holds good approximately for helium and argon. Electron polarization and diamagnetic susceptibility are related to each other through screening constant. PAULING[8] calculated the screening constants by taking into consideration the major penetration effects, the theoretical and experimental values of diamagnetic susceptibility for helium and neon were comparable (9) The direct calculations of Σr^2 using Thomas-Fermi charge distribution do not give promising results as the electrons for other orbitals, to which Thomas-Fermi approximation does not hold make major contributions to susceptibility

---

[1] BHATNAGAR S. S. and K. N. MATHUR, *Physical Principles and Applications of Magnetochemistry*, p. 130. Macmillan, London (1935).

[2] J. A. POPLE, *J. Chem. Phys.* **37**, 53 (1962).

[3] J. H. VAN VLECK, *Phys. Rev.* **29**, 349 (1927), **31**, 587 (1928).

[4] S. S. BHATNAGAR and K. N. MATHUR, *Phil. Mag.* **5**, 536 (1928); **6**, 217 (1928); *J. Indian Chem. Soc.* **6**, 303 (1929).

[5] L. N. MULAY, *Proc. Indian Acad. Sci.* (1951) **34 A**, 245 (1951).

[6] Y. MATSUNAGA and H. AKAMATSU, *Bull. Chem. Soc. Japan*, **26**, 364 (1953).

[7] J. P. VINTI, *Phys. Rev.* **42**, 813 (1932).

[8] L. PAULING, *Proc. Roy. Soc.* **A114**, 181 (1927).

In the present communication a simple semi-empirical correlation is obtained between the electron polarization and diamagnetic susceptibility According to VAN VLECK(1)

$$\chi_M \qquad \frac{Ne^2}{6mc^2}\sum_i \bar{r}_i^2 \tag{1}$$

which can be simplified to

$$\chi_M \qquad \frac{Ne^2}{6mc^2} \quad f \quad r^2 \tag{2}$$

where f is the effective number of electrons contributing to diamagnetic susceptibility moving in orbits of radius r The semi-empirical dispersion equation is given by[10]

$$P_E = \frac{Ne^2}{3\pi m} \quad \frac{F}{\nu_0^2 \quad \nu^2} \tag{3}$$

where F is the number of the so called dispersion electrons From Equations (2) and (3)

$$\frac{\chi_M}{P_E} \quad \frac{\pi f}{2F} r^2 \left[\frac{\lambda^2 \quad \lambda_0^2}{\lambda_0^2\lambda^2}\right]$$

$$\simeq \frac{\pi f}{2F}\frac{r^2}{\lambda_0^2}(\lambda_0^2 - \lambda^2) \tag{4}$$

If we assume that λ_0^2 is linearly related to $\frac{fr^2}{F}$ a linear relationship between electron polarization and diamagnetic susceptibility is expected Figures 1 and 2 show the validity of the assumption for rare gases, alkali metal ions, alkaline earth ions, halogen ions and simple ionic crystals (11) A closely homologous series of ions and salts of these ions with the same anion lie on the same straight line It is interesting to note that the plot corresponding to anions has less slope while the plots for cations are with higher slopes as compared to rare-gas plot The points corresponding to ions deviate from the mean straight line while the points corresponding to salts are well on the mean straight line These deviations are probably due to the polarization effects which distort the relationship between the component group property and the total molecular property from linearity (12)

---

(9) J C SLATER, *Phys Rev* **32,** 349 (1928)

(10) W KAUZMANN, *Quantum Chemistry* Academic Press, New York (1957)

(11) Data for Fig 1 and Fig 2 are taken from
a C H D CLARK, *The Fine Structure of Matter* Part II p 298, Chapman and Hall, London (1938)
b K IKENMEYER, *Ann Phys* 1169 (1929)
c O FOEX, G J GORTER and L J SMITS, *Constantes Selectionnees Diamagnetisme et Paramagnetisme, Relaxation Paramagnetique*, Union Internationale de chimie, Paris

(12) a J R PARTINGTON, *Advanced Treatise on Physical Chemistry*, Vol 4, Longmans, London (195
b V S JATKER, S K K JATKER and A J MUKHEDKAR, *Z physik Chem* **36,** 221 (1963)

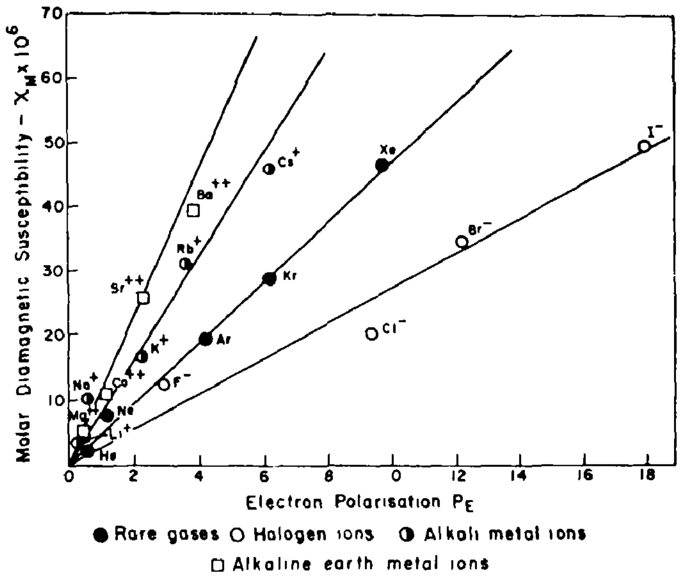

Molar Diamagnetic Susceptibility – χ_M x 10^6
0
10
20
30
40
50
60
70
Electron Polarisation P_E
0
2
4
6
8
10
12
14
16
18
He
Li+
Ne
Mg++
Na+
Ca++
F−
K+
Ar
Sr++
Rb+
Kr
Ba++
Cs+
Xe
Cl−
Br−
I−
● Rare gases ○ Halogen ions ◑ Alkali metal ions
□ Alkaline earth metal ions

FIG. 1

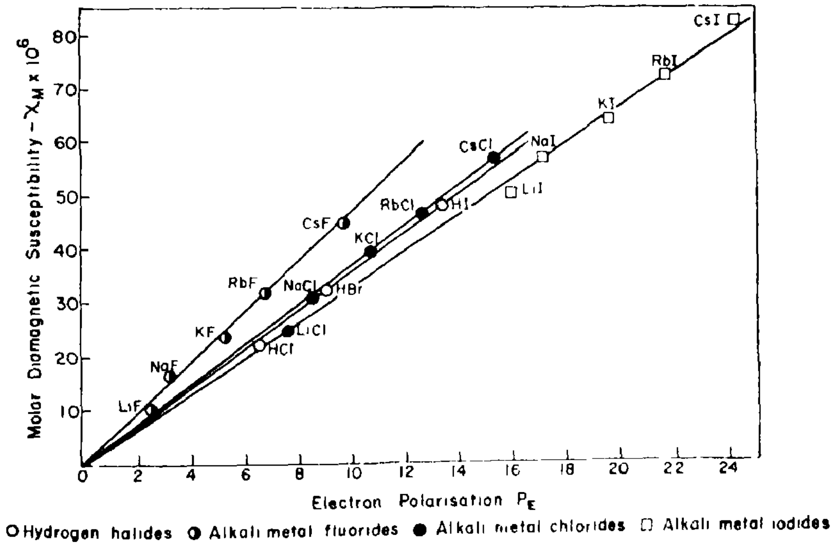

Molar Diamagnetic Susceptibility – χ_M x 10^6
10
20
30
40
50
60
70
80
Electron Polarisation P_E
0
2
4
6
8
10
12
14
16
18
20
22
24
LiF
NaF
KF
RbF
CsF
HCl
LiCl
NaCl
HBr
KCl
RbCl
HI
CsCl
NaI
LiI
KI
RbI
CsI
○ Hydrogen halides ◑ Alkali metal fluorides ● Alkali metal chlorides □ Alkali metal iodides

FIG. 2

Table 1 summarizes the values of the effective number of dispersion electrons determined from refractive dispersion data and the calculated values of the radius of the orbital of the electron contributing to diamagnetic susceptibility on the assumption

$$f = F \tag{5}$$

It is interesting to note that the calculated values of the radii are of the same order as the atomic radii calculated from atom refractions and van der Waals radii. One can therefore conclude that the so called dispersion electrons play an important role in diamagnetic susceptibility. This observation leads to a linear relation between f and λ_0, to a first approximation (refer Equation 4). A similar linear relation was observed[14] between the chromophoric length and absorption maxima which are related to λ_0 for complex organic molecules.

TABLE 1

	He	Ne	Ar	Kr
Effective number of dispersion electrons f *	1.02	2.31	4.61	4.93
Characteristic wavelength λ_0 (Å)	513.9	489.0	707.7	842.5
Van der Waals radii[13]	0.93	1.12	1.54	1.69
Atomic radii calculated from atom refraction	0.80	0.99	1.60	1.84
Atomic radii (present work)	0.81	1.01	1.2	1.64

* Calculated from the refractive dispersion data taken from *International Critical Tables of Numerical Data*, National Research Council. McGraw-Hill, London (1930).

Acknowledgement—Our thanks are due to the Council of Scientific and Industrial Research (India) for the award of a Junior Research Fellowship to one of us (V. S. J.).

---

[13] L. PAULING, *Nature of Chemical Bond*, p. 514. Cornell University Press (1960).

[14] E. A. BRAUDE, *Chemistry of Carbon Compounds*, Edited by E. H. RODD, Vol. IA, p. 71. Elsevier, Amsterdam (1951).

J. Inorg. Nucl. Chem. 1963. Vol. 25, pp. 1375 to 1381. Pergamon Press Ltd. Printed in Northern Ireland

STABILITY OF IRON (III) CHELATE OF CRESOTIC ACIDS. A SPECTROPHOTOMETRIC STUDY OF IRON (III) m-CRESOTIC ACID CHELATE

S. S. Katiyar and V. B. S. Chauhan
Department of Chemistry, Indian Institute of Technology, Kanpur (India)

(*Received* 15 *October* 1962; *in revised form* 22 *March* 1963)

Abstract—Iron (III) forms a reddish chelate with m-cresotic acid (RH), which exhibits maximum absorption at 530 mμ. The chelate was found to be stable in the pH range 1.5–4.5. The composition of the iron (III)–*m*-cresotic acid chelate corresponded to 1:1 when investigated by the slope ratio, mole ratio and continuous variation methods. The stability constant of the complex at pH 1.93, 2.90 and 3.92 was 5.00, 4.67 and 3.68 respectively.

Cresotic acids (*o*-*m* and *p*) are known to form complexes with a number of cations.[1–7] Recently they have been used as complexometric indicators in the titrimetric determination of iron[8,9] against EDTA. The end point is indicated by the change, to light yellow, of the violet colour of the iron (III) *m*-cresotate complex in acidic solution. The nature, composition and stability of the iron (III) *m*-cresotate complex form the subject matter of this communication.

EXPERIMENTAL

Materials

m-cresotic acid. B.D.H. (L.R.) sample was purified[10] by several crystallizations from ethanol. The final product used for preparing solutions of the sodium salt had a m.p. 179°C (literature value 178°C).[11]

Ferric ammonium sulphate. The standard solution of E. Merck (G.R.) grade reagent was prepared as described by Vogel. It was standardized by the thioglycollate method.[12]

Sodium acetate and hydrochloric acid. These chemicals needed for the preparation of buffers were of AnalaR quality from E. Merck. The stock solutions of the buffers were kept in polythene bottles.

Apparatus

Absorption measurements. The optical measurements were made with a Beckman DU spectrophotometer using 10 mm corex cells. The temperature in the cell compartment was maintained at

---

[1] A. K. Bhattacharya and G. S. Rao, *J. Sci. Industr. Res.* (India) **18 B**, 351 (1959).

[2] S. P. Agarwal, R. C. Agarwal and T. N. Srivastava, *Z. Analyt. Chem.* **171**, 91 (1959).

[3] S. C. Tripathi and S. Prakash, *J. Indian Chem. Soc.* **35**, 139 (1958).

[4] M. S. Kachhwaha and A. K. Bhattacharya, *J. Ind. Chem. Soc.* **39**, 397 (1962).

[5] V. V. Subanna and A. K. Bhattacharya, *Analyt. Chim. Acta* **23**, 145 (1960).

[6] S. C. Tripathi and S. Prakash, *Z. Phys. Chem.* **208**, 181 (1958).

[7] L. Sommer, *Z. Analyt. Chem.* **171**, 420 (1960).

[8] C. S. Pande and T. S. Srivastava, *Z. Analyt. Chem.* **175**, 29 (1960).

[9] S. S. Katiyar and V. B. S. Chauhan, Unpublished data, April 1962.

[10] I. Heilbron and H. M. Bunbury (Editors), '*Dictionary of Organic Compounds*,' p. 336. Eyre and Spottiswoode, London (1946).

[11] C. D. Hodgman, R. C. Weast and S. M. Selby, *Hand Book of Chemistry and Physics*, p. 935. The Chemical Rubber Publishing Co., Cleveland, Ohio (1960).

[12] A. I. Vogel, *A Textbook of Quantitative Inorganic Analysis*, p. 647. Longmans Green, London (1960).

the desired value (35.5°C) with the help of a dual thermospacer set, this last was connected to an externally maintained Hopler's ultrathermostat.

pH measurements. The pH of the solutions was measured with the help of a Cambridge bench pattern pH meter operated by a 12 V battery.

RESULTS AND DISCUSSION

Nature of the complex. The method suggested by VOSBURGH and COOPER,(13) was employed. Various mixtures containing 1.6×10^{-4} M iron and varying amounts of *m*-cresotate in the range 1.6–4.8×10^{-4} M, were prepared and their spectrum recorded. The results obtained are represented graphically in Fig. 1. Here curves 1, 2, 3 refer to the spectra of solutions containing Fe (III) and reagent in the ratio 1 : 1, 1 : 2, 1 : 3 at pH = 2.88. Since the absorption by iron (III) and *m*-cresotic acid is zero in the visible range of the spectrum, it may be assumed that the λ_{max} observed is due to the presence of the complex. It can be seen from this figure that the maximum absorption occurs at the same wavelength i.e. 530 mμ for all mixtures, which indicates the formation of only one complex species.

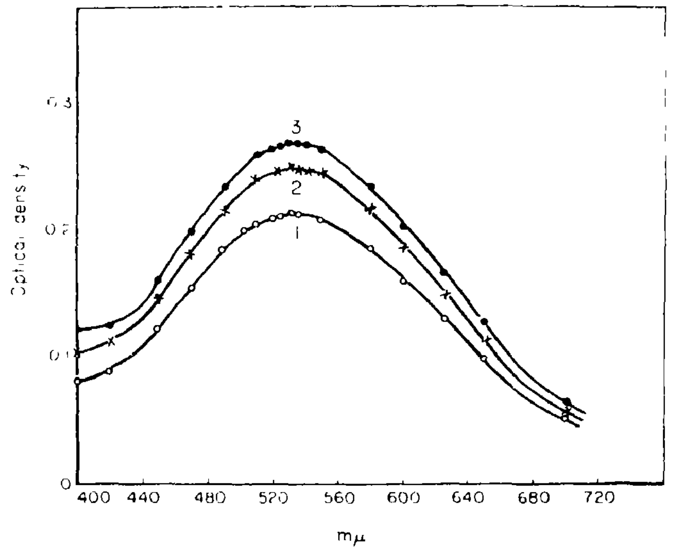


FIG. 1.—Absorption spectra of solutions containing iron (III) and *m*-cresotic acid [Fe (III) : acid for curve 1 = 1 : 1, curve 2 = 1 : 2, curve 3 = 1 : 3]

Influence of pH on the stability of complex. Fig. 2 represents the typical data obtained on the variation of absorbance with pH. The optical density of solutions containing constant quantity of iron (III) (1.6×10^{-4} M) and sodium *m*-cresotate (4.8×10^{-4}) in presence of different buffers in the range 1.04–5.24 were recorded at 530 mμ. Fig. 2 shows that the optimum pH range for the formation of the complex is between 2.00–4.00.

Beer's law. The applicability of Beer's law to the reddish violet complex was examined. Fig. 3 records the typical data obtained for the variation of optical density with concentration of the complex. The concentration of complex was taken equal to the concentration of the iron (III) in the presence of excess *m*-cresotic acid. The value of ϵ at pH 2.90 corresponded to 1.61×10^{3} litre mole^{-1} cm^{-1}.

---

(13) W. C. VOSBURGH and G. R. COOPER, *J. Amer. Chem. Soc.* **63**, 437 (1941).

J. Inorg. Nucl. Chem. 1963. Vol. 25, pp. 123 to 127. Pergamon Press Ltd. Printed in Northern Ireland

THE SYSTEMS NaCl–CrCl$_3$ AND KCl–CrCl$_3$

C. M. COOK, Jr.*
Pigments Department, E. I. du Pont de Nemours & Co. Inc.
Wilmington, Delaware

(*Received* 30 *March* 1962; *in revised form* 21 *June* 1962)

Abstract—Phase diagrams of the NaCl–CrCl$_3$ and KCl–CrCl$_3$ systems show the congruently melting compounds Na$_3$CrCl$_6$, K$_3$CrCl$_6$, and K$_3$Cr$_2$Cl$_9$. Room temperature X-ray patterns of K$_3$Cr$_2$Cl$_9$ show this compound to be isomorphous with the previously known Cs$_3$Cr$_2$Cl$_9$.

CHROMIUM(III) compounds tend strongly towards six-fold co-ordination because of the 12 D_q crystal field stabilization energy† acquired when Cr^{3+} is surrounded by an octahedral configuration of anions. There is evidence that octahedral co-ordination of Cr(III) occurs in both crystalline and liquid CrCl$_3$-alkali chloride mixtures. Thus the structure of Cs$_3$Cr$_2$Cl$_{9(c)}$ is that of 2 Cr(III)'s surrounded octahedrally by Cl$^-$'s with the octahedra sharing a common face.(2) The absorption spectrum of dilute solutions of CrCl$_3$ in molten LiCl–KCl exhibits maxima consistent with the presence of octahedrally co-ordinated Cr(III).(3) A recent study of the effects of temperature on this spectrum(4) shows the octahedral co-ordination to persist to at least 1000°C, in contrast to the more weakly stabilized VCl$_3$(5) and TiCl$_3$(4) solutions where the spectra indicate transformation from octahedral to tetrahedral co-ordination as the melt temperature increases above 600–800°C.

The liquid–solid phase diagrams of the CrCl$_3$–NaCl and KCl systems were determined in a search for six-co-ordinated compounds suggested by the above evidence.

EXPERIMENTAL

NaCl and KCl were fused under HCl and were crushed and stored in a dry atmosphere. Anhydrous CrCl$_3$ was prepared by chlorination of Cr (99.8 per cent purity) at 900°. This CrCl$_3$, obtained as a bulky sublimate, was freed of trace oxychloride by COCl$_2$ treatment, was densified by sintering at 900°C under Cl$_2$, and was loaded into the sample bulb. After addition of alkali chloride, the mixture was melted under Cl$_2$, cooled under argon, and the bulb evacuated and sealed.

Mixture compositions were calculated from the initial weights of Cr and alkali chloride and were confirmed by analyses of the samples after use. For $0 < X_{CrCl_3} < 0.2$ the uncertainty in X_{CrCl_3} is ± 0.005; for $X_{CrCl_3} > 0.4$ the uncertainty is ± 0.02.

Heating and cooling curves of the samples were determined in a rocking furnace by a differential temperature measurement procedure.(6) CrCl$_3$-rich melts exhibited considerable super-cooling before crystallization; accordingly the transition temperatures were, where possible, located from heating curves. Liquidus temperature reproducibility was within ±3° except for $X_{CrCl_3} > 0.4$.

After the cooling curve determination, samples of CrCl$_3$–MCl mixtures were ground in a dry-box, sealed into 0.5 mm Lindemann glass capillaries, and exposed to vanadium filtered chromium radiation in an X-ray powder camera. The *d*-spacings were read with a Mies scale, and line intensities were estimated visually.

---

* Present address: Operations Evaluation Group, Office of the Chief of Naval Operations, Navy Dept., Washington, D.C.

† D. S. MCCLURE,(1) reports for Cr^{3+} surrounded octahedrally by Cl$^-$ the D_q = 1330 cm^{-1}. Thus the CFSE ~ 45 kcal/mole.

(1) D. S. MCCLURE, *Solid State Phys.* **9,** 426 (1959).

(2) G. J. WESSEL and D. J. W. IJDO, *Acta Cryst.* **10,** 466 (1957).

(3) G. HARRINGTON and B. R. SUNDHEIM, *Ann. N.Y. Acad. Sci.*, **79,** 11, 950 (1960). Also B. R. SUNDHEIM, Private communication (1962).

(4) D. M. GRUEN, Unpublished work (1961).

(5) D. M. GRUEN and R. L. MCBETH, *J. Chem. Phys.* **66,** 57 (1962).

(6) C. M. COOK, Jr., *J. Phys. Chem.* **65,** 1505 (1961).

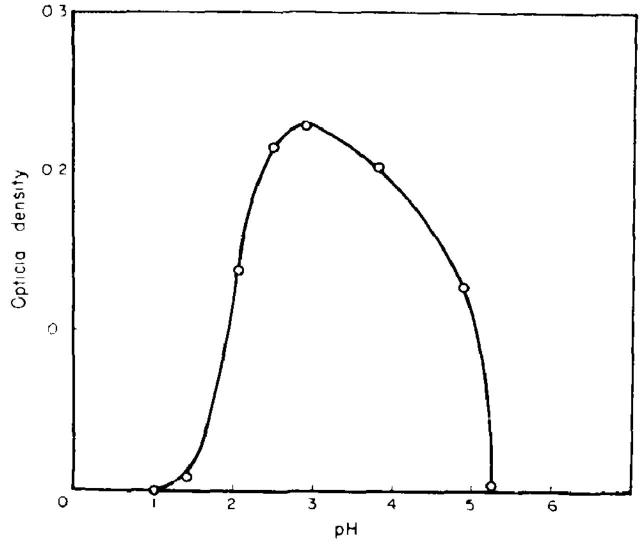


Fig. 2 — Variation of absorbance at 530 mμ with pH of solutions

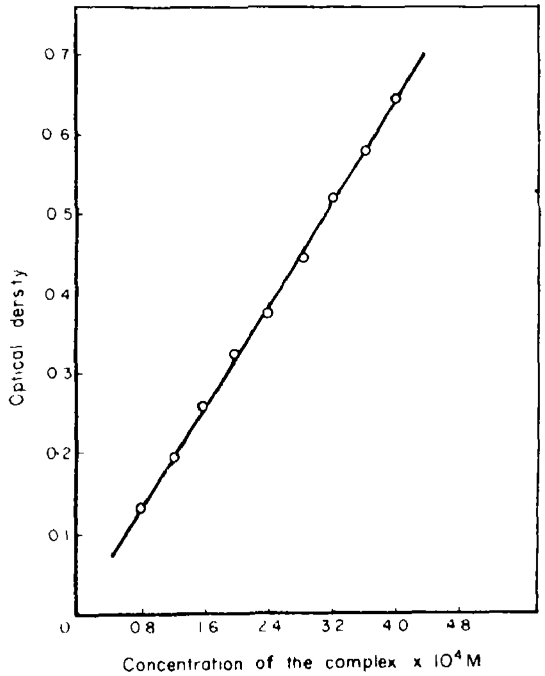


Fig. 3 Variation of absorbance with concentration of the complex λ 530 mμ

Composition of the chelate The stoichiometry of the components involved in the formation of the chelate was ascertained by the following methods

The continuous variation method⁽¹⁴⁾ This method was applied using equimolar solutions The concentrations of iron (III) and sodium *m*-cresotate were varied in the range 0 8 10^{-4} M to 7 2 10^{-4} M and 7 2 × 10^{-4} M to 0 8 × 10^{-4} respectively,

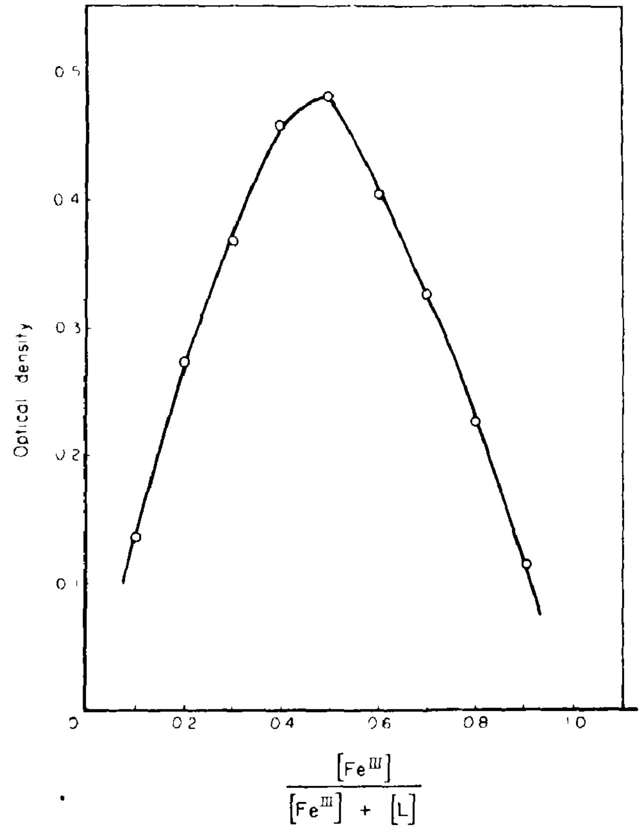


FIG 4 — Determination of composition of the complex by Job's method of continuous variation (λ 530 mμ)

keeping the total concentration of iron (III) and ligand constant for all readings The pH of all the solutions was maintained at 2 88 and the optical density measurements were made at λ = 530 mμ Typical observations are plotted in Fig 4 It is seen that the maxima in this figure occur at 0 5 mole fraction of iron (III) which shows that composition of the chelate is 1 1

The slope ratio method This elegant method introduced by HARVEY and MANNING⁽¹⁵⁾ gives conclusive information regarding the composition of the complex from the slopes of the plots obtained by varying the concentration of one component when the other is in excess and vice versa The concentration of the constant component was kept 8 × 10^{-4} M while that of the other was varied in the range 0 8 10^{-4} M to 4 8 × 10^{-4} M The bulk concentration of cresotic acid could not exceed 8 × 10^{-4} M due to appearance of turbidity The absorbance measurements at

---

⁽¹⁴⁾ P JOB, *Ann Chim* **9**, 113 (1928), **16**, 97 (1936)

⁽¹⁵⁾ A E HARVEY and D L MANNING, *J Amer Chem Soc* **72**, 4488 (1950)

$\lambda = 530$ mμ and pH = 2 88, are recorded in Fig 5 Curve 1 refers to the condition when *m*-cresotic acid was kept constant while for 2 the variable component was *m*-cresotic acid The ratio of the slopes of the plots 2 to 1 works out to be 1 15 which approximates to unity, thus indicating the formation of 1 1 complex

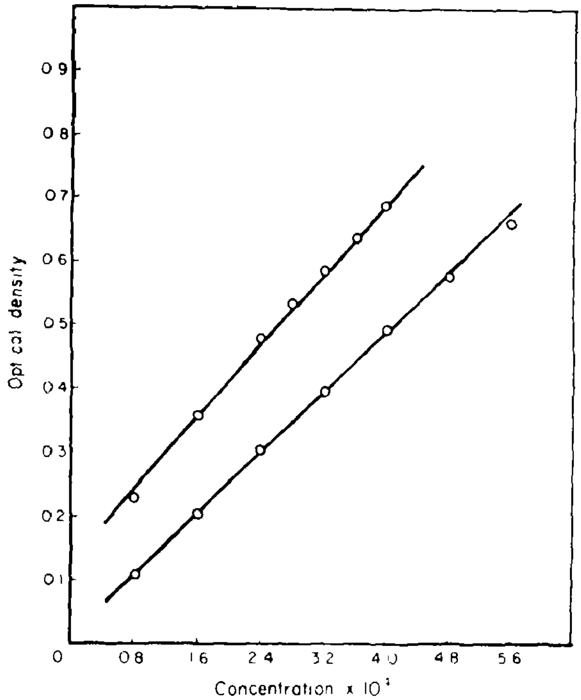


FIG 5 Determination of composition of the complex by slope ratio method at 530 mμ (curve for plot 2 shifted upwards by 1 cm on the ordinate) Lower curve 1 upper curve, 2

The mole ratio method The applicability of this method proposed by YOE and JONES,[16] to the iron (III) *m*-cresotate chelate is shown in Fig 6 Curve 1 of this figure was obtained when the concentration of iron (III) was kept constant and the iron (III) to reagent ratio was varied between 1 0 05 to 1 8, the pH being maintained at 2 88 However, due to the ionization of the complex in dilute solutions a sharp break is not obtained But when the absorbance measurements of the same solutions were made in the presence of 5 ml of 1 0 M KCl a break was observed, as seen in curve 2 It is interesting to observe that the break occurs at a ratio of 1 mole of the reagent to 1 mole of iron (III), suggesting thereby the formation of a 1 1 complex

Stability constant of the chelate and its variation with pH The computation of the classical formation constant (k) of the iron (III) *m*-cresotate chelate at different pH was done from the Job curves obtained at pH 1 93 2 90 and 3 92 reported in Fig 7, using the extinction coefficient measured for the complex above and taking the ionization constant of the acid as 6 84 × 10^{-4} at 25°C

---

[16] J H YOE and A L JONES *Industr Engng Chem*, *Analyt Ed* **16**, 111 (1946)

The last column of Table 1 gives the values of the thermodynamic stability constant (K) computed with the aid of the Debye-Huckel equation(17)

$$\log K = \log k + \frac{2AZ_AZ_B\sqrt{\mu}}{1+\sqrt{\mu}} \qquad (6)$$

TABLE 1

pH	Ionic strength	Classical stability constant log k	Thermodynamic stability constant log K
1 93	0 23	5 00	6 01
2 90	0 21	4 67	5 65
3 92	0 20	3 68	4 64

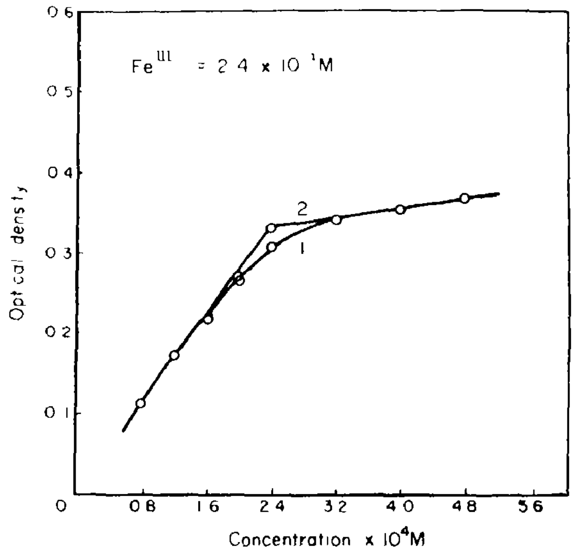
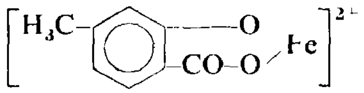


FIG. 6 Composition of the complex by mole ratio method λ - 530 mμ

The value of ΔF° at 35 5°C for the *m*-cresotic acid iron (III) chelate works out to be −7 98 kcals

The chelatometric properties of *m*-cresotic and salicylic acid are due to the presence of a hydroxyl and carboxylic group in γ position to each other By analogy with the salicylate complex(18) the structure of the iron (III) complex of *m*-cresotic acid may be represented as



However, a comparison of the stability constants of the *m*-cresotate and salicylate complexes which are respectively 4 67 and 17 4 (log *k*), reveals a considerable lowe

---

(17) S GLASSTONE, *A Textbook of Physical Chemistry* p 970 Macmillan, London (1956)

(18) A K BABKO, *Zavodskaya Lab* **13**, 645 (1947)

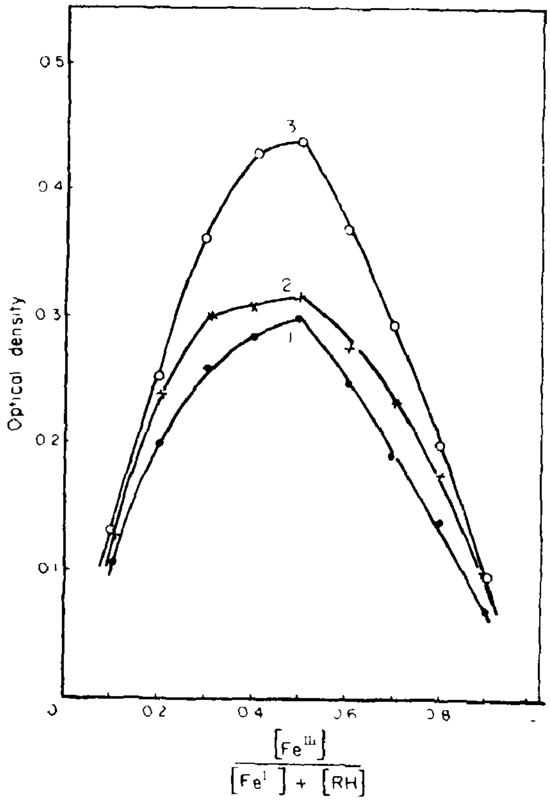


FIG. 7 Job's continuous variation curves at different pH [Curve 1 pH 1.93, curve 2 pH 3.92 and curve 3 pH 2.90.]

in log k value by the introduction of the CH_3 group. A similar lowering in stability constant of the iron (III) salicylate complex was observed by FOLEY and ANDERSON,[19] when an SO_3H group was introduced in the benzene ring of the salicylic acid. This is evident from the stability constant of the iron (III) 5-sulphosalicylic acid complex, which is 3.68. Similarly the stability constant of the complex formation between iron (III) and *o*-cresotic acid[20] is lower.

Acknowledgements—The authors wish to express their gratitude to Prof. P. K. KELKAR, Director, Indian Institute of Technology, Kanpur for his kind interest in the work and to Director, National Sugar Institute for the permission to use the spectrophotometer. They would like to also thank Dr. A. B. SEN for encouragement.

[19] R. T. FOLEY and R. C. ANDERSON, *J. Amer. Chem. Soc.* **70**, 1195 (1948).

[20] S. S. KATIYAR and V. B. S. CHAUHAN, *Z. Anorg. Chem.* **323**, 28 (1963).

J. Inorg. Nucl. Chem. 1963, Vol. 25, pp. 1383 to 1388. Pergamon Press Ltd. Printed in Northern Ireland

INFRA-RED SPECTRUM AND STRUCTURE OF DI-CYCLOPENTADIENYL DI-IRON TETRACARBONYL

K. Noack
Cyanamid European Research Institute, Cologny/Geneva

(*Received* 2 *April* 1963)

Abstract—A re-investigation of the infra-red spectrum of $[C_5H_5Fe(CO)_2]_2$ in the carbonyl region in different solvents has shown that the compound is very unstable in chlorinated solvents. In chloroform solution the three bands at 2003, 1958 and 1769 cm^{-1} disappear and three new bands at 2058, 2011 and 1721 cm^{-1} appear. All these new bands coincide with reported Raman bands. Since the infra-red spectrum shows no temperature dependence between +30° and −110°C isomeric forms can be excluded. A structure in keeping with these results is proposed.

There is some confusion in the literature about the interpretation of the infra-red and Raman spectra of di-cyclopentadienyl di-iron tetracarbonyl (I).(1) The reported spectra in different solvents vary markedly and the Raman spectrum shows one coincidence with the infra-red bands in the carbonyl stretching region. The compound is centrosymmetrical(2) in the solid form and has been shown to possess a dipole moment in solution.(3)

We have reinvestigated the infra-red spectrum in different solvents and at different temperatures, as well as in KBr with the aim of finding new evidence to explain these discrepancies.

EXPERIMENTAL

The di-cyclopentadienyl di-iron tetracarbonyl was prepared according to Hallam *et al.*(4)

Infra-red spectra were measured on a Perkin Elmer Mod. 221 infra-red spectrophotometer equipped with NaCl prism-grating exchange unit and a linear absorbance potentiometer. The spectral slit width in the investigated region was about 1.5 cm^{-1} (slit programme 880). The spectrometer was calibrated with carbon monoxide and water vapour. The frequencies are accurate to ±0.5 cm^{-1}.

The cells for the solution spectra were 0.1 and 0.01 cm thick respectively. The cool-cell for the low temperature measurement will be described elsewhere.(5)

RESULTS

Figure 1 shows the spectrum of di-cyclopentadienyl di-iron tetracarbonyl (I) in heptane and Fig. 2 several spectra in chloroform solution. In heptane solution the compound is relatively stable, only the weak band 2015 cm^{-1} increased its intensity with time, and is therefore due to a decomposition product. From Fig. 2 it follows clearly that the sample is reacting with or decomposed by the chloroform. The strong bands, at 2003, 1958 and 1772 cm^{-1}, shown also in the spectrum in heptane solution, disappear and three new bands at 2056, 2014 and 1715 cm^{-1} appear with time.

---

(1) F. A. Cotton, H. Stammreich and G. Wilkinson, *J. Inorg. Chem. Nucl.* **9**, 3 (1959).

(2) O. S. Mills, *Acta Cryst.* **11**, 620 (1958).

(3) F. Weiss, W. Hubel and R. Merenyi, *Chem. Ber.* **95**, 1155 (1962).

(4) B. F. Hallam, O. S. Mills, P. L. Pauson, *J. Inorg. Nucl. Chem.* **1**, 313 (1955).

(5) K. Noack, *Spectrochim. Acta* (In press).

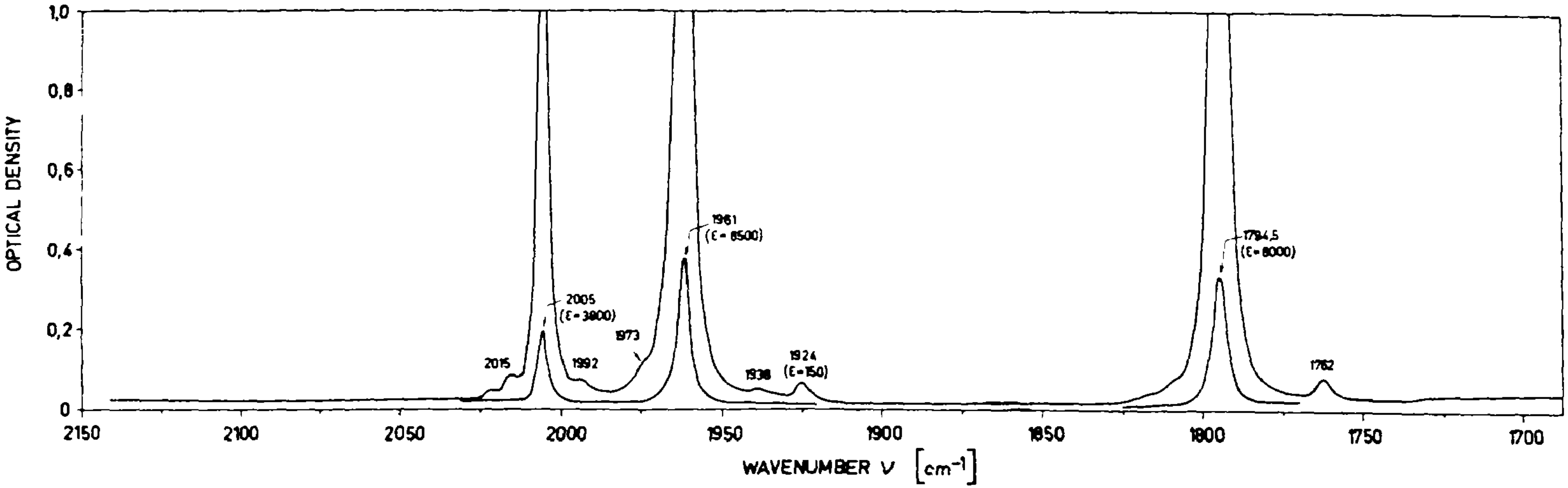


Fig 1 —Infra-red spectrum of $[C_5H_5Fe(CO)_2]_2$ in heptane solution

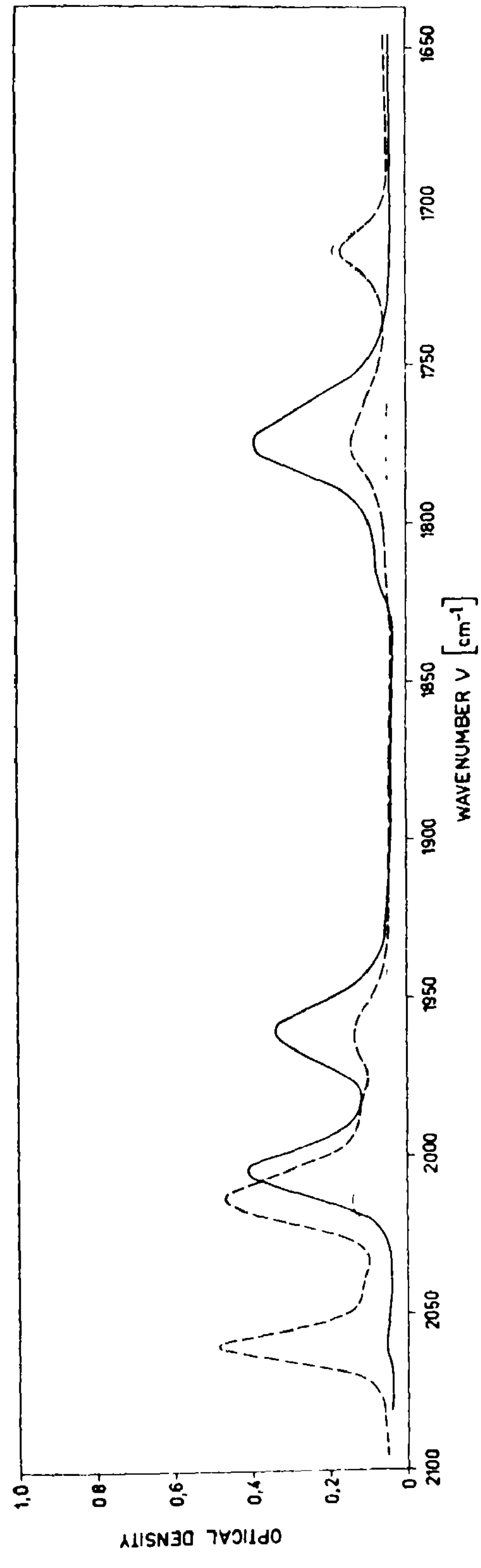


Fig. 2.—Infra-red spectra of $[C_5H_5Fe(CO)_2]_2$ in chloroform solution

—— immediately after making up the solution

- - - - after 1 hr

after 12 min irradiation with Hg-lamp

With a silicon filter between the sample and the light source of the spectrometer, this decomposition is very much slower From the Fig 2 it can be seen that by irradiation with a mercury lamp the two new bands at 2056 and 2014 cm^{-1} also disappear, whereas the one at 1715 cm^{-1} is not affected These bands belong, therefore, to different compounds Similar results obtained in other solvents are listed in Table 1 In all the solvents different bands appear with time, but they are not exactly at the same frequencies and the reaction products are certainly different Only the reaction with chloroform has been studied in detail

TABLE 1 CARBONYL BANDS OF $[C_5H_5Fe(CO)_2]_2$ IN DIFFERENT SOLVENTS
(The bands appearing with time are in bold face)

Solvent	Frequency [cm^{-1}]						
Heptane			2005	1961		1794,5	
Chloroform	**2056**	**2014**	2003	1958		1772	**1715**
CCl_4	**2055**	**2011**	2004	1958	**1811**	1782	
Pyridine	**2068**	**2038**	1988	1948	**1933**	1774	**1722**
Ethanol	**2036**	1995	**1982** sh	1956	1810	1785	1755 sh

A chloroform solution was irradiated with a tungsten lamp until the original bands had disappeared and then evaporated to dryness A red crystalline residue with an infra-red spectrum identical with the one reported by PIPER *et al* for cyclopentadienyl iron di-carbonyl chloride[6] was obtained

To check for a possible equilibrium of isomeric forms of different geometry, as discussed by COTTON *et al*,[1] infra-red spectra in pentane and CS_2 solutions were run at several temperatures from room temperature down to −110 C No change in the relative intensities could be detected in either solvent The explanation of the behaviour of the compound on the basis of an equilibrium of different geometrical isomers is therefore, ruled out

The infra-red spectrum was repeated in KBr and it was observed that one can, by careful and long enough (15 min) grinding, obtain a clear disk with a spectrum similar to the solution spectra After several minutes, the disk becomes suddenly opaque and a new spectrum results identical to the one reported by COTTON *et al*[7] By regrinding and repressing the same disk this cycle can be repeated Fig 3 shows both spectra, together with a spectrum in Nujol which has the same bands as the opaque KBr disk The two kinds of KBr disks give, with the exception of the carbonyl bands, identical spectra from 4000 to 650 cm^{-1}

DISCUSSION

With the data available at the time, COTTON *et al*[1] could not rationalise the Raman and infra-red spectra with the physical properties of I The Raman spectrum normally of great help in the elucidation of structures of highly symmetrical molecule consisted of five bands, of which only one coincided with an infra-red band

A comparison with Table 1 suggests immediately that the Raman bands at 206 2019 and 1721 cm^{-1} are due to a reaction product with the solvent

---

[6] T S PIPER, F A COTTON and G WILKINSON, *J Inorg Nucl Chem* **1**, 165 (1955)

[7] F A COTTON, A D LIEHR and G WILKINSON, *J Inorg Nucl Chem* **1**, 175 (1955)

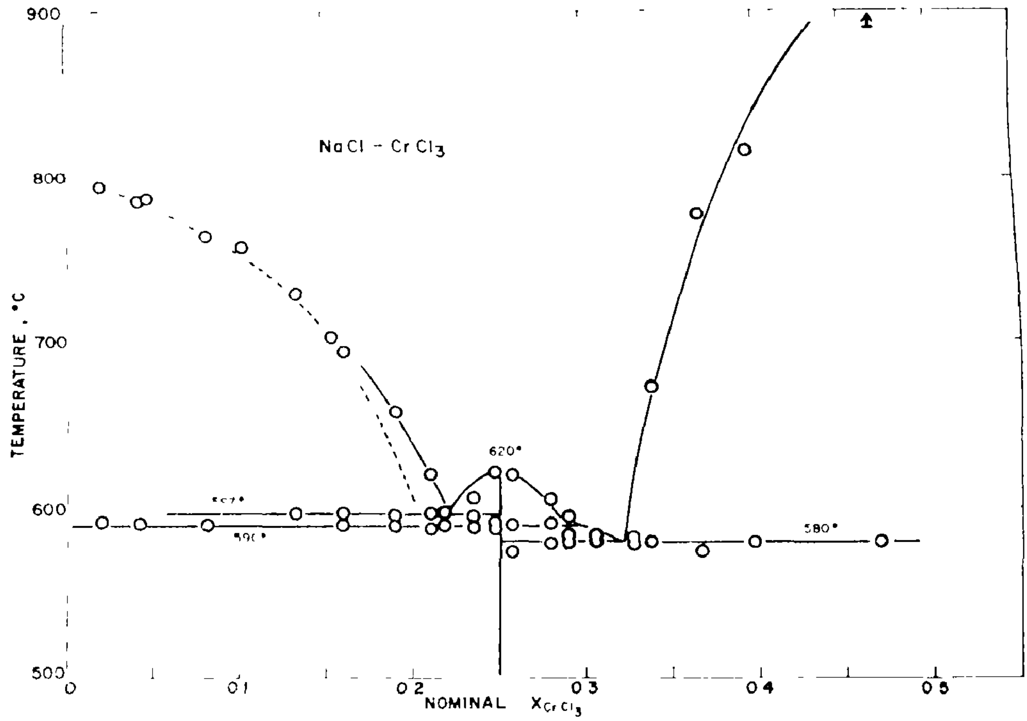


FIG. 1 Partial solid liquid phase diagram of the system, NaCl-$CrCl_3$
- - Calculated liquidus if Cr(III) as $CrCl_6^{3}$

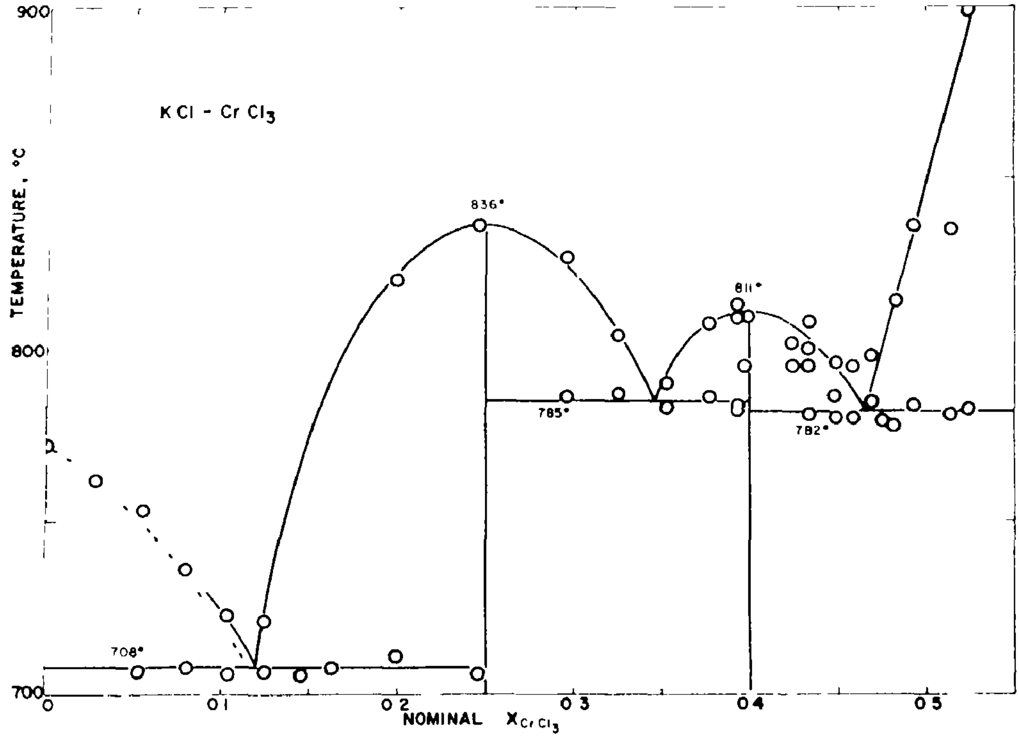


FIG 2 Partial solid liquid phase diagram of the system, KCl-$CrCl_3$
- - Calculated liquidus if Cr(III) as $CrCl_6^{3}$

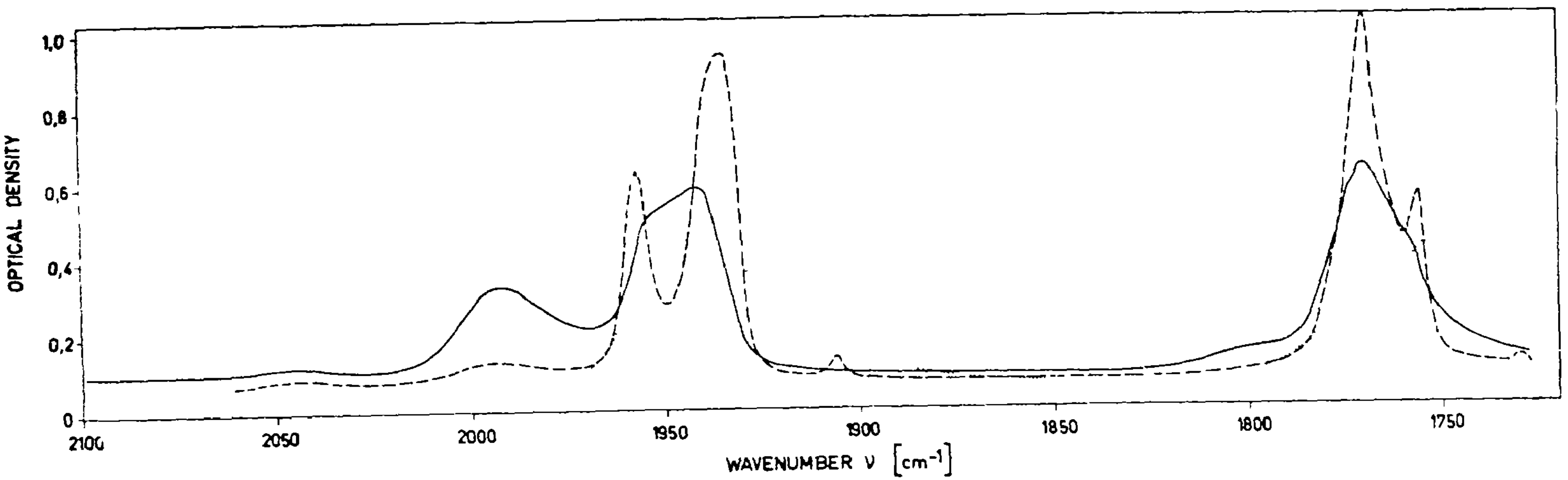


FIG. 3 — Infra-red spectra of $[C_5H_5Fe(CO)_2]_2$

——— clear KBr disk
- - - - transformed KBr disk
Nujol-mull

The only Raman band certainly due to undecomposed I is the one at 1958 cm^{-1}, coinciding with the strongest infra-red band

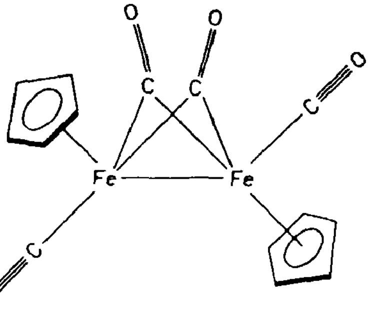
In higher concentrations in heptane several very weak (ε 150) bands and shoulders appear in the infra-red spectrum (see Fig 1) Three of them, by their frequencies and intensities are the ^{13}C-isotopic bands of the three strong peaks (1973, 1924 and 1762 cm^{-1}) and two very weak satellites cannot be simply explained Because of their low intensity they are probably not due to a fundamental vibration

TABLE 2 —Raman spectrum of $[C_5H_5Fe(CO)_2]_2$ (after reference (1) The most certain bands are underlined) (In $CHCl_3$, pyridine and alcohol)

2064 (3b)	2019 (2)	1958 (6)	1737 (3)	1721 (5)

These observations make the assignment of the spectra somewhat easier The infra-red spectrum of I shows in solution three strong carbonyl bands, two for the terminal and one for the bridging carbonyls At least one of these is clearly coincident with a Raman line and there are no positive Raman lines which are not coincident with the infra-red bands A centrosymmetrical structure for the molecule in solution can, therefore, be ruled out

This is also in agreement with the dipole moment of 3 10 Debye (3) As shown in Fig 3, I dispersed in KBr gives two different spectra, one similar to the solvent, the other identical with the Nujol-mull spectrum The Nujol-mull and the one KBr spectrum are characteristic for the solid, for which a centrosymmetrical structure has been established by X-ray analysis (2) As has been discussed by COTTON *et al* (1) this spectrum is compatible with the centrosymmetrical structure, because the molecules occupy two different sites in the crystal In solution, the molecules have lost their centre of symmetry and are distorted The most probable structure is one with C_s symmetry



The bands at 2003 and 1958 cm^{-1} belong to the two non equivalent terminal carbonyls, and the band at 1786 cm^{-1} to the two identical bridging carbonyls From the selection rules one would expect also two bridging carbonyl bands, but they could coincide if the coupling between the two groups is small, or the symmetrical motion could lead to a band too weak to be detected The integrated intensity of this one band can well account for two bridging carbonyls (8)

Acknowledgements—I have to thank Dr E A C LUCKEN, Dr E WEISS and Dr H D MURDOCH for many stimulating discussions

(8) K NOACK, *Helv Chim Acta* **45**, 1847 (1962)

J. Inorg. Nucl. Chem. 1963. Vol. 25, pp. 1389 to 1393. Pergamon Press Ltd. Printed in Northern Ireland

THE INFRA-RED SPECTRA OF METAL(II)-HYDRAZINE COMPLEXES

L. SACCONI and A. SABATINI

Istituto di Chimica Generale e Inorganica della Università di Firenze,
Via Jacopo Nardi 39, Firenze, Italy

(*Received* 28 *February* 1963; *in revised form* 1 *May* 1963)

Abstract—The infra-red spectra of some hydrazine metal complexes of the general formula $M(N_2H_4)_2Cl_2$ have been measured in the 2–35 μ region. A comparison of the spectra of $Cd(N_2H_4)_2Cl_2$ and $Cd(N_2D_4)_2Cl_2$ enables the assignment of the observed absorption bands. The sequence of some of the molecular modes of vibration (such as the NH_2 twisting, rocking, torsion and the N—N and M—N stretching frequencies) agrees closely with the natural order of the stability of bivalent complexes.

MANY stable complexes of metal salts with one, two or three hydrazine molecules are known, but their structure so far received very little attention. The only available complete crystal structure is that of FERRARI *et al.*(1) on the $Zn(N_2H_4)_2Cl_2$ compound. This structure is characterized by infinite chains of —$M(N_2H_4)_2M$— groups. Such a structure requires hydrazine molecules to act as non-chelating ligands as previously suggested by SCHWARZENBACH *et al.*(2)

On the other hand, it is only recently the structure of gaseous hydrazine itself has been clarified. Theoretical calculations by PENNEY and SUTHERLAND(3) have shown that hydrazine should exist in the *gauche* form with the two NH_2 groups at 90° to each other. This has been confirmed by YAMAGUCHI *et al.*(4) who have studied the far infra-red spectrum of hydrazine.

X-rays studies on solid hydrazine seem to favor the existence of the eclipsed *cis* and *gauche* forms.(5)

In the present paper we have examined the infra-red absorption spectra of a series of hydrazine metal complexes with the general formula $M(NH_2\text{–}NH_2)_2Cl_2$ (M = Mn, Fe, Co, Ni, Cu, Zn and Cd) in the 2–35 μ region. The aim of this work was to study:

(1) the configuration of the hydrazine molecule in these complexes, and

(2) the influence of the different metal ions on the spectra of the complexes.

This class of compounds seemed very suitable for such an investigation because the Debyegrams revealed that they are isomorphous so that the lattice effects should be analogous throughout the series.

EXPERIMENTAL

Preparation of compounds. Divalent manganese, cobalt, iron, nickel, zinc and cadmium complexes were prepared according to the literature.(6) The copper complex prepared by the method described by HOFFMANN and MARBURG[7] is not pure enough Better results are obtained by adding hydrazine to anhydrous cupric chloride ground under chloroform in a mortar The resulting blue compound is then filtered in a dry atmosphere and desiccated under vacuum at 50° *Anal* $Mn(N_2H_4)_2Cl_2$ N% calc 29 54, N% found 29 48, $Fe(N_2H_4)_2Cl_2$ N% calc 29 36, N% found 29 21, $Co(N_2H_4)_2Cl_2$ N% calc 28 90, N% found 28 95, $Ni(N_2H_4)_2Cl_2$ N% calc 28 93, N% found 29 38, $Cu(N_2H_4)_2Cl_2$ N% calc 28 22, N% found 28 25, $Zn(N_2H_4)_2Cl_2$ N% calc 28 00, N% found 27 75, $Cd(N_2H_4)_2Cl_2$ N% calc 22 69, N% found 22 76

---

(1) A. FERRARI, A. BRAIBANTI and G. BIGLIARDI, *Acta Cryst.* **16**, 498 (1963).

(2) G. SCHWARZENBACH and A. ZOBRIST, *Helv. Chim. Acta* **35**, 1291 (1952).

(3) W. G. PENNEY and G. B. B. M. SUTHERLAND, *J. Chem. Phys.* **2**, 492 (1934).

(4) A. YAMAGUCHI, I. ICHISHIMA, T. SHIMANOUCHI and S. MIZUSHIMA, *J. Chem. Phys.* **31**, 843 (1959).

(5) R. L. COLLIN and W. N. LIPSCOMB, *Acta Cryst.* **4**, 10 (1951).

(6) H. FRANZEN and O. VON MAYER, *Z. Anorg. Chem.* **60**, 247 (1908).

Preparation of the Cd-deutero-compound Approximately 1 g of hydrazine hydrochloride was placed in a glass tube containing 5 ml of 99 8% D_2O and the stoppered tube was allowed to stand overnight at room temperature Its contents were then frozen by surrounding the tube with a dry-ice-acetone bath The tube was then attached to a vacuum pump, the system evacuated and the water removed from the sample by condensing it in an adjacent tube surrounded by a dry-ice acetone bath A second 5 ml portion of D_2O was then added to the solid hydrochloride and the entire procedure repeated After four such exchanges the final solid product is believed to be primarily the desired deuterated hydrochloride This was then ground with about 0 5 g of CdO and the mixture put into a small flask kept at 95° for about 24 hours To the final product 5 ml of D_2O were added and the whole filtered and washed with 5 ml of D_2O in small portion In the final product a small quantity of unreacted CdO was still present

Absorption measurements The infra-red spectra were obtained using a Perkin-Elmer, Model 21 infra-red spectrophotometer, equipped with NaCl and CsBr prisms, and a Perkin-Elmer Model 12 C single beam spectrophotometer fitted with a LiF prism The samples were examined as suspension in Nujol and, for the 1200–1500 cm^{-1} and LiF region, as suspensions in hexachlorobutadiene

TABLE 1 —FREQUENCIES (CM^{-1}) AND ASSIGNMENTS FOR METAL HYDRAZINE COMPLEXES

Assignment	$MnCl_2$ $2N_2H_4$	$FeCl_2$ $2N_2H_4$	$CoCl_2$ $2N_2H_5$	$NiCl_2$ $2N_2H_4$	$CuCl_2$ $2N_2H_4$	$ZnCl_2$ $2N_2H_4$	$CdCl_2$ $2N_2H_4$	$CdCl_2$ $2N_2D_4$	ν_H/ν_D
NH_2 stretching	3298 *s*	3291 *s*	3288 *s*	3288 *s*	3258 *s*	3262 *s*	3294 *s*	2467 *s*	1 34
NH_2 stretching	3237 *s*	3232 *m*	3225 *m*	3230 *m*	3190 *m*	3214 *m*	3235 *m*	2380 *m*	1 36
NH_2 stretching	3151 *w*	3146 *w*	3134 *w*	3146 *w*	3146 *w*	3134 *w*	3151 *w*	2323 *w*	1 35
								1213 *vw*	
NH_2 bending	1606 *s*	1607 *s*	1605 *s*	1608 *s*	1608 *s*	1611 *s*	1609 *s*	1183 *s*	1 36
NH_2 bending	1575 *s*	1575 *s*	1568 *m*	1568 *m*	1567 *m*	1575 *s*	1583 *s*	1165 *m*	1 36
NH_2 wagging	1348 *w*	1351 *w*	1347 *w*	1342 *w*	1338 *vw*	1349 *w*	1352 *w*	1050 *w*	1 29
NH_2 wagging	1299 *w*	1307 *w*	1308 *w*	1313 *w*	1322 *w*	1312 *w*	1297 *w*	1013 *m*	1 28
		1179 *sh*	1190 *m*	1201 *m*	1227 *w*	1190 *sh*			
NH_2 twisting	1156 *s*	1164 *s*	1172 *s*	1172 *s*	1198 *s*	1175 *s*	1150 *s*	851 *s*	1 35
		1156 *sh*	1152 *sh*						
								977 *vw*	
N—N stretching	960 *m*	964 *m*	974 *w*	978 *m*	985 *w*	976 *m*	963 *m*	957 *m*	1 01
								925 *w*	
								887 *vw*	
								820 *m*	
NH_2 as rocking	590 *m*	607 *m*	625 *m*	649 *m*	682 *m*	625 *m*	593 *m*	451 *m*	1 31
NH_2 sym rocking	518 *s*	553 *s*	582 *s*	613 *s*	658 *s*	580 *s*	517 *s*	400 *s*	1 29
M—N stretching	343 *m*	369 *m*	388 *m*	409 *m*	440 *m*	385 *m*	338 *m*	306 *m*	
						345 *w*			

---

[7] K A HOFFMANN and F C MARBURG, *Ann* **305**, 214 (1899)

RESULTS AND DISCUSSION

Vibrational assignment The proposed assignment of the observed infra-red frequencies for the metal hydrazine complexes is given in Table 1

Three bands are observed in the 3 μ region, obviously due to NH_2 stretching vibrations These bands occur at a frequency of about 50–100 cm $^{-1}$ lower than the corresponding ones of gaseous hydrazine [8] The observed frequency decrease is of the same order of magnitude as that found in the case of the ammine-complexes [9] This weakening of the N–H bonds can easily be explained as resulting from the electron drainage from the nitrogen atom, due to its coordination to the metal

The bands observed at about 1600 cm $^{-1}$ can be assigned with confidence to the NH_2 bending vibrations

For the assignment of the NH_2 wagging and twisting vibrations, which are expected in the region between 1350–900 cm $^{-1}$ it is convenient to first discuss the spectrum of the cadmium complex for which the deuterated analogue is available and then to extend the assignment thus gained to the other complexes

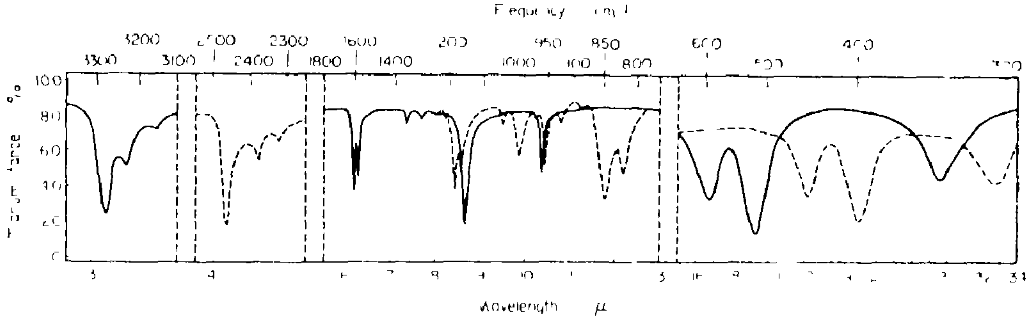


FIG. 1 —Infra-red spectra of $CdCl_2 \cdot 2N_2H_4$ (—) and of $CdCl_2 \cdot 2N_2D_4$ ( )

Four bands are observed in this region at 1352, 1296, 1150 and 963 cm $^{-1}$ By deuteration the first three are considerably shifted towards low frequencies, while the fourth remains practically at the same frequency (Fig 1) This fact undoubtedly places the N–N stretching vibration at 963 cm $^{-1}$ The choice between the remaining three bands is rather a puzzle In aliphatic amines[10,11] the wagging vibrations occur at about 900 cm $^{-1}$ as extremely intense bands Furthermore this type of vibration is strongly anharmonic so that they are shifted by isotopic substitution with a ratio of about 1 26–1 28 For the metal-complexes where the lone pair electrons of the nitrogen atom are engaged in the bond with the metal atom, one may expect the wagging vibration to be shifted towards higher frequencies On the other hand the NH_2 twisting vibrations are known to be generally weak in the infra-red spectrum and to accur at a much higher frequency than the wagging modes [2,10,11]

It is clear from Table 1 that none of the three previously mentioned bands fulfills the expectation completely For instance, if we choose the two weak bands at 1352 and 1297 cm^{-1} as wagging vibrations, it is hard to explain the 1150 cm^{-1} band as a twisting one because of its intensity On the other hand, if we assume the 1150 cm^{-1} band to be a wagging vibration, then it is difficult to attribute to twisting vibrations the observed isotopic shift of 1 28 and 1 29 However, the first choice is preferred because the argument of the isotopic shift is considered to be more important than the one of band intensity Therefore the strong band that occurs between 1150 and 1200 cm^{-1} in the spectra of the complexes studied is assigned to a twisting vibration and the two weak bands at about 1350 and 1300 cm^{-1} to the wagging modes

---

[8] P A GIGUÈRE and I D LIU, *J Chem Phys* **20**, 136 (1952)

[9] J CHATT, L A DUNCANSON and L M VENANZI, *J Chem Soc* 4461 (1955)

[10] A P GRAY and R C LORD, *J Chem Phys* **26**, 690 (1957)

[11] A SABATINI and S CALIFANO, *Spectrochim Acta* **16**, 677 (1960)

Only in the spectra of the Cd(II) and Mn(II) complexes do the bands at about 1150 cm^{-1} appear as a single peak In all other cases the band has one or even two shoulders probably due to impurities For instance, a shoulder appears in the spectrum of $Zn(N_2H_4)_2Cl_2$ precipitated from ammoniacal solution but it is absent when the compound is obtained from anhydrous alcoholic solution of $ZnCl_2$ and hydrazine

In the region between 500 and 700 cm^{-1} all the compounds examined show two absorption bands The observed isotopic shift in the case of the cadmium complex clearly indicates that they are due to NH_2 motions The one at higher frequency has been assigned to the asymmetric rocking of the NH_2 groups and the other at lower frequency to the symmetric NH_2 rocking vibration

The following considerations support this assignment In free hydrazine the NH_2 torsion has been observed$^{(3)}$ at 376 7 cm^{-1} In hydrazine complexes, however, this vibration goes in an asymmetric rocking mode and therefore its frequency should increase Actually, we would expect the frequency to be higher than that of the symmetric rocking mode because of the presence of a potential barrier hindering the rotation of the NH_2 groups around the N—N bond

On the basis of the conclusion reached by BARROW$^{(12)}$ and MIZUSHIMA$^{(13)}$ for the metal ammonia complexes, the bands in the 300–500 cm^{-1} region have been assigned to the M—N stretching vibration Again this assignment is supported by a comparison of the spectrum of the Cd(II) complex with that of the deuterated analogue since the observed shift ratio is not greater than 1 10 as we would expect for such a vibration$^{(12,14)}$

The crystal structure of the Zn complex$^{(1)}$ shows that the hydrazine molecule is very likely in the "staggered" form with C_2 symmetry For such a configuration four NH_2 stretching and two NH_2 twisting modes should be infrared active In the IR spectrum therefore one NH_2 stretching and one NH_2 twisting absorption bands are missing A satisfactory explanation for this cannot be suggested

Effect of cation on the vibrational frequencies Table 1 shows that many observed frequencies as the NH_2 twisting, sym rocking and as rocking as well as the N—N and M—N stretching ones vary according to the well known "Irving Williams" order of stability of the bivalent metal complexes$^{(15)}$ Mn $<$ Fe $<$ Co $<$ Ni $<$ Cu $>$ Zn $>$ Cd

The effect is particularly regular for the above mentioned vibrations, but a general trend can always be observed Table 1 also shows that the two NH_2 stretching bands at higher frequency, with the exception of the nickel complexes, decrease in a regular way as the stability of the complexes increases

---

(12) G M BARROW, R H KRUEGER and F BASOLO, *J Inorg Nucl Chem* **2**, 340 (1956)

(13) E P BERTIN, I NAKAGAWA, S MIZUSHIMA, J J LANE and J V QUAGLIANO, *J Amer Chem Soc* **80**, 525 (1958)

(14) S MIZUSHIMA, I NAKAGAWA and J V QUAGLIANO, *J Chem Phys* **23**, 1367 (1955)

(15) H IRVING and R P WILLIAMS, *Nature, Lond* **162**, 746 (1948), *J Chem Soc* 3192 (1953)

Probably second order effect, like hydrogen bonds, solid state effects and mechanical coupling of vibrations are responsible for the irregular trend observed for one wagging vibration as well as for the third NH_2 stretching and for the bending vibrations

Acknowledgements—Thanks are expressed to the "Consiglio Nazionale delle Richerche" and to the C N E N for financial support

J. Inorg. Nucl. Chem. 1963. Vol. 25, pp. 1395 to 1396. Pergamon Press Ltd. Printed in Northern Ireland

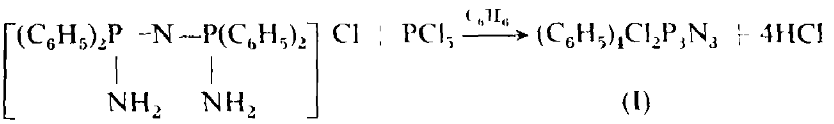
THE SYNTHESIS OF 1,1-DICHLORO-3,3,5,5-TETRAPHENYLCYCLOTRIPHOSPHONITRILE FROM A LINEAR PHOSPHONITRILE

C. D. SCHMULBACH and C. DERDERIAN
Department of Chemistry, The Pennsylvania State University, Pennsylvania

(Received 9 April 1963)

Abstract—The value of a general method for synthesizing cyclic phosphonitrile polymers from linear polymers is illustrated by the synthesis of 1,1-dichloro-3,3,5,5-tetraphenyltriphosphonitrile from $(C_6H_5)_4P_2N_3H_4Cl$ and phosphorus pentachloride.

THE existence of linear phosphonitrile polymers is reasonably established.(1) The use of stable *linear* phosphonitriles in the syntheses of cyclic polymer phosphonitriles has been given no attention. The value of such an approach is illustrated in the case of the preparation of 1,1-dichloro-3,3,5,5-tetraphenyltriphosphonitrile (I). The preparation of this compound in 16 per cent yield by the method of Friedel-Craft has been reported.(2) This method involves long reaction times, requires meticulous care in isolation procedures and results in a rather modest yield. Compound (I), m.p. 141–142.5°C, has been prepared in this laboratory in 88 per cent yield by cyclization of the linear polymer $(C_6H_5)_4P_2N_3HCl$(3,4) according to the equation



$$\left[(C_6H_5)_2\underset{NH_2}{\underset{|}{P}}-N-\underset{NH_2}{\underset{|}{P}}(C_6H_5)_2\right]Cl + PCl_5 \xrightarrow{C_6H_6} (C_6H_5)_4Cl_2P_3N_3 + 4HCl$$

(I)

The synthesis of 1,1-dichloro-3,3,5,5-tetraphenyltriphosphonitrile is of particular significance in that it illustrates the value of a general method for preparing cyclic compounds which can be synthesized only with difficulty by other methods. A corollary to such a method of synthesis is that it allows construction of isomers of specific stereochemistry in carefully controlled stepwise-fashion. Compound (I) is of particular interest for kinetic studies in that it contains a single phosphorus atom at which nucleophilic substitution can occur.

Compound (I), which is readily recrystallized from acetonitrile, forms a 1:1 adduct with acetonitrile. The adduct loses 1 mole of acetonitrile at approximately 80°C and then melts sharply at 141–142.5°C. The infrared spectrum of compound (I) shows the characteristic sharp P–N vibration bands at 1208 cm^{-1} and 1162 cm^{-1} and bands at 1430 cm^{-1} and 995 cm^{-1} which are assigned to P-phenyl bonds.(5)

---

(1) C. D. SCHMULBACH, *Progress in Inorganic Chemistry* (Edited by F. A. COTTON) Vol. 4, p. 275. Interscience, New York, (1962).
(2) R. A. SHAW and F. B. G. WELLS, *Chem. & Industr.* (London) 118 (1960).
(3) I. I. BEZMAN and J. H. SMALLEY, *Chem. & Industr.* (London) 839 (1960).
(4) H. H. SISLER, H. S. AHUJA and N. L. SMITH, *Inorg. Chem.* **1**, 84 (1962).
(5) L. J. BELLAMY, *The Infra-red Spectra of Complex Molecules*, p. 320. J. Wiley, New York (1960).

Materials

Technical grade diphenylchlorophosphine was generously supplied by the Victor Chemical Works and was used without further purification. Chlorine gas and ammonia were obtained from the Matheson Co. The ammonia gas was dried by condensing on sodium metal and was then distilled into the reaction vessel. All organic reagents which were technical grade and were obtained from the Fisher Scientific Company were dried and fractionally distilled before using. Phosphorus pentachloride (Reagent Grade) was obtained from Fisher Scientific Company and was used without further purification.

Procedure

The compound $(C_6H_5)_4P_2N_3H_4Cl$ was prepared according to the method of BEZMAN and SMALLEY[3] with slight modification, according to the reaction

$$2(C_6H_5)_2PCl_3 + 8NH_3 \xrightarrow{CHCl_3} (C_6H_5)_4P_2N_3H_4Cl + 5NH_4Cl$$

The ammonium chloride was removed by filtration and the filtrate retained. The solid remaining on the filter paper was rinsed with water to remove the ammonium chloride, washed with ether, and then air dried. This portion of crude $(C_6H_5)_4P_2N_3H_4Cl$ was added to the larger portion obtained in the next step. To the chloroform filtrate mentioned earlier was added a large volume of anhydrous ether which resulted in the precipitation of crude $(C_6H_5)_4P_2N_3H_4Cl$. The crude $(C_6H_5)_4P_2N_3H_4Cl$ was recrystallized from acetonitrile to give large colourless needle crystals, m.p. 244.5–246.0°C, in 85 per cent yield. The melting point, infrared spectrum, and elemental analyses agree with published data.[3,4]

To a stirred suspension of 20.2 g (0.0447) of $(C_6H_5)_4P_2N_3H_4Cl$ in 1000 ml of benzene at reflux temperature was added slowly over 4 hr 9.30 g (0.0447 mole) of phosphorus pentachloride in 100 ml of benzene. A stream of dry nitrogen gas was passed through the system. The reaction mixture was refluxed for 24 hr. After cooling to room temperature, 2.37 g of solid unreacted $(C_6H_5)_4P_2N_3H_4Cl$ was removed by filtration and the benzene layer evaporated to dryness to give a white crystalline solid consisting of unreacted phosphorous pentachloride and compound (I). After subtracting the theoretical weight for unreacted phosphorous pentachloride from the total weight of crude reaction mixture, the conversion of $(C_6H_5)_4P_2N_3H_4Cl$ to compound (I) was observed to be essentially quantitative. The white solid was recrystallized from acetonitrile, dried for 6 hr under vacuum at the boiling point of chloroform, to give 17.91 g of colourless crystals of 1,1-dichloro-3,3,5,5-tetraphenyltriphosphonitrile, m.p. 141–142.5°C (uncorrected), 142–143°C reported.[2] This represents an 88 per cent yield based on the quantity of $(C_6H_5)_4P_2N_3H_4Cl$ consumed. Found: C, 56.25; H, 4.07; N, 8.08; P, 18.08; Cl, 13.79%; Mol. wt. 531 (cryoscopic in benzene). Calcd. for $(C_6H_5)_4Cl_2P_3N_3$: C, 56.05; H, 3.92; N, 8.17; P, 18.07; Cl, 13.79%; Mol. wt. 515.

A KBr pellet was used in obtaining the infrared spectrum of compound (I).

Since the 1:1 adduct of 1,1-dichloro-3,3,5,5-tetraphenyltriphosphonitrile and acetonitrile slowly dissociates, even on standing at room temperature, its melting point could not be determined. The existence of the adduct was established by chemical analyses and molecular weight determination. (Found: C, 56.92; H, 4.23; N, 10.00%; Apparent mol. wt. 275 (cyoscopic in benzene). Calc. for $(C_6H_5)_4Cl_2P_3N_3 \cdot CH_3CN$: C, 56.23; H, 4.17; N, 10.08%; Apparent mol. wt. 278.)

DISCUSSION

Both NaCl and KCl form, with $CrCl_3$, congruently melting M_3CrCl_6 compounds, c.f. Fig. 1 and 2. The X-ray powder diagrams, Fig. 3, for Na_3CrCl_6 and K_3CrCl_6 are dissimilar, and these compounds do not appear to be isostructural at room temperature. Na_3CrCl_6 undergoes a solid-state transition at 590°, an effect not shown by the K_3CrCl_6 compound.

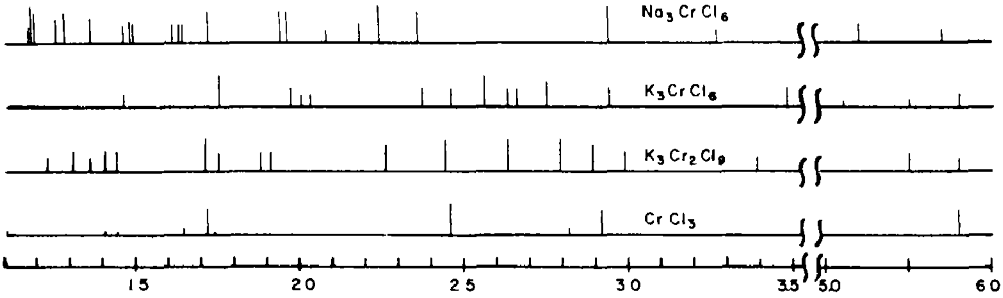


FIG. 3.—*d*-Spacings of major lines of Cr(III)-containing compounds in MCl–$CrCl_3$ systems.

The congruently melting $3KCl \cdot 2CrCl_3$ compound exhibits hexagonal symmetry with $a = 6.88$ Å, $c = 17.52$ Å and is isomorphous with $Cs_3Cr_2Cl_9$. The $3NaCl \cdot 2CrCl_3$ compound was not observed, powder patterns of those NaCl–$CrCl_3$ compositions with $0.35 < X_{CrCl_3}$ showing lines only of Na_3CrCl_6 and $CrCl_3$.

The steep rise of the liquidus of the NaCl–$CrCl_3$ system with $X_{CrCl_3} > 0.32$ indicates the solid phase to be higher melting and less soluble than would be anticipated for $Na_3Cr_2Cl_9$. If the solid phase in this composition region is $CrCl_{3(c)}$, as indicated by the room temperature X-ray patterns, at temperatures above 900°C substantial pressures of $Cl_{2(g)}$ and $CrCl_{4(g)}$ should be generated by displacement of the equilibria

$$CrCl_{3(c)} = CrCl_{2(l)} + \tfrac{1}{2}Cl_{2(g)} \qquad (1)$$

and

$$2CrCl_{3(c)} = CrCl_{2(l)} + CrCl_{4(g)} \qquad (2)$$

to the right by solution of $CrCl_{2(l)}$ in the melt.* Sample bulbs containing NaCl–$CrCl_3$ mixtures with $X_{CrCl_3} > 0.45$ were observed to explode at ca. 920° before reaching liquidus temperatures.

The apparent non-existence of $Na_3Cr_2Cl_9$, contrasted with the congruent melting behaviour of $K_3Cr_2Cl_9$, demonstrates a rather marked increase in complex compound stability upon going from the Na^+ to K^+ cation. The melting behaviour of $Cs_3Cr_2Cl_9$ would determine whether this trend in stability continues to the larger Cs^+ ion.

In agreement with the spectral indications of $CrCl_6^{3-}$ stability,(4) the liquidus lines of NaCl and KCl-rich compositions indicate $CrCl_6^{3-}$ to be the principal Cr(III)-containing species in the molten alkali chloride solutions near the freezing point. If it

---

* For these reactions the estimated $K \sim 10^{-2}$ at 920°C. Since the sample bulb contains 0.2–0.3 g atoms Cr(III) and has free volume $\sim 25\ cm^3$, internal pressures of several atmospheres can be anticipated in the presence of $CrCl_{3(c)}$.

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 1397 to 1400. Pergamon Press Ltd. Printed in Northern Ireland

THE RELATIVE RATES OF REACTION OF TRIMERIC AND TETRAMERIC PHOSPHONITRILIC HALIDES WITH *n*-PROPYLAMINE

T. MOELLER and S. G. KOKALIS*
Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois

(*Received* 19 *March* 1963)

Abstract—A conductimetric kinetic analysis of the aminolysis of the phosphonitrilic halides $(NPF_2)_{3\text{ and }4}$, $(NPCl_2)_{3\text{ and }4}$ and $(NPBr_2)_{3\text{ and }4}$ by *n*-propylamine in acetonitrile at 25° indicates a second-order rate-determining step in each instance. From data for the second-order constants (k_2) and the pseudo first-order constants (k'_1) the comparative order of reactivity is $(NPBr_2)_4 > (NPBr_2)_3 \sim (NPCl_2)_4 > (NPCl_2)_3 \sim (NPF_2)_4 > (NPF_2)_3$.

ALTHOUGH reactions of the phosphonitrilic halides (esp. chlorides) with primary alkyl amines have been utilized for synthesis,[1-6] no quantitative correlations of rates of aminolysis have been established. Kinetic studies have been limited to the polymerization of the tetrameric chloride,[7,8] to the reaction of the trimeric chloride with aniline in ethanol,[9] and to the reaction of the trimeric chloride with piperidine in toluene.[10] In the last of these studies, mixed second- and third-order kinetics were observed for the formation of the mono-piperidino derivative, and it was noted that the tetrameric chloride reacts much more rapidly with an amine than does the trimeric chloride.

Inasmuch as the interpretation of d_π-p_π aromatic character in these ring systems is of general interest, an insight into the effect of both ring complexity and electronegativity of the halogens present on the availability of *d*-orbitals from the phosphorus atoms for nucleophilic attack is of interest. Kinetic data essential to such an approach can be obtained conductimetrically since the aminehydrohalide product of the aminolysis reaction is ionic. For convenience, the reactions studied were limited to those of n-propylamine.

EXPERIMENTAL

Materials. Commercial trimeric and tetrameric phosphonitrilic chlorides obtained from Hooker Chemicals Corporation were purified by recrystallization to materials melting at 114° and 123°.

---

* Louderman Chemical Laboratories, Washington University, St. Louis, Mo.

(1) S. G. KOKALIS, K. JOHN, T. MOELLER and L. F. AUDRIETH, *J. Inorg. Nucl. Chem.* **19**, 191 (1961).

(2) M. BECKE-GOEHRING, K. JOHN and E. FLUCK, *Z. anorg. Chem.* **302**, 103 (1959).

(3) K. JOHN, T. MOELLER and L. F. AUDRIETH, *J. Amer. Chem. Soc.* **82**, 5616 (1960); **83**, 2608 (1961).

(4) D. LIPKIN, *U.S. Pat.* No. 2192921 (1940).

(5) S. K. RAY and R. A. SHAW, *Chem. and Industr.* 53 (1959); *Proc. Chem. Soc.* 26 (1960); *J. Chem. Soc.* 872 (1961).

(6) M. YOKOYAMA, *Nippon Kagaku Zasshi* **81**, 1453 (1960).

(7) F. PATAT and K. FROMBLING, *Monatsh.* **86**, 718 (1955).

(8) J. O. KONECNY, C. M. DOUGLAS and M. Y. GRAY, *J. Polymer Sci.* **42**, 383 (1960).

(9) J. V. BAILEY and R. E. PARKER, *Chem. and Industr.* 1823 (1962).

(10) B. CAPON, K. HILLS, and R. A. SHAW, *Proc. Chem. Soc.* 390 (1962).

respectively The phosphonitrilic bromides were prepared as previously described(11) and were recrystallized from *n*-heptane The fluorides were obtained by reaction of the chlorides with sodium fluoride in nitrobenzene (12) Purified n-propylamine was refluxed over and then distilled from potassium hydroxide pellets Acetonitrile was distilled four times from fresh phosphorus (V) oxide Its conductivity was within the range 5 9 10^{-8} Ω cm $^{-1}$ at 25 cited for samples containing less water than is detectable with Karl Fischer reagent (13)

Apparatus All conductance measurements were made at 25 0 + 0 1° with an Industrial Instruments Inc , bridge, Type RC-16B, operating at 1000 c/s The conductance cell contained platinized 2 0 3 0 cm platinum electrodes and had a capacity of 65 ml A ground-glass stopper excluded moisture The cell constant was 0 147 cm $^{-1}$

Procedure Since it was established independently that no complicating reactions occur and that freshly prepared solutions of the reactants ($(NPX_2)_n$ and n $C_3H_7NH_2$) in anhydrous acetonitrile have negligible conductance, only the amine hydrohalide, n-$C_3H_7NH_3{}^+X^-$, produced during aminolysis was responsible for observed conductance Standard 10^{-2} or 10^{-3} M solutions of the reactants were used These were brought to thermal equilibrium in the thermostat before mixing Mixing was effected in the conductance cell by adding a measured volume of one reactant with a syringe to a measured volume of the other A stopwatch was started at the instant of mixing, and resistance was then measured at suitable time intervals It was found desirable to record resistance each minute for the first 10 min and then at increasingly long intervals up to 100 min The resistance observed after 100 hr was considered to be that for complete reaction (R_∞)

Successive dilutions of the original stock solutions to one-tenth the original concentration were used to provide additional reaction systems Consistency in procedural details permitted correlation of reaction rates among the phosphonitriles studied

RESULTS AND DISCUSSION

The overall order of the aminolysis reaction was determined in each instance by the variation-in-ratio-of-reactants method (14) It was found essential to use 10^{-5} 10^{-6} M solutions of the reactants to achieve less than 10 per cent reaction within the first 5-10 min of study Based upon the generalized rate expression

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k[(NPX_2)_{3\ 4}]^m[\text{n-}C_3H_7NH_2]^n \qquad (1)$$

the order as so determined for each reactant is summarized in Table 1 The values of *m* and *n* approach unity in all cases within experimental error The graphical method of PESSEN(15) was used to determine the total order of the reaction, *N* When 10^{-2}, 10^{-3} or 10^{-4} M solutions were used, reasonably linear plots of the quantity $R_t/(R_t - R_\infty)$ vs time were obtained for all of the phosphonitrilic halides studied These are in agreement with a second-order rate-determining step for the aminolysis reaction Pertinent data are summarized in Table 2

Rate constants were derived from half-life data (Table 3) by PESSEN's graphical method and a pseudo first-order calculation (16) The pseudo k_1' values (Table 3) were based upon the first 3 min of reaction with the amine in 30–40 mole ratio excess The k_2' values were obtained by dividing k_1' values by the concentrations of the amine, *a*

---

(11) K JOHN and T MOELLER, *J Inorg Nucl Chem* **22**, 199 (1961)

(12) T MOELLER, K JOHN and F Y TSANG, *Chem and Industr* 347 (1961)

(13) W S MUNEY and J F COETZEE, *J Phys Chem* **66**, 89 (1962)

(14) F DANIELS and R A ALBERTY, *Physical Chemistry*, p 330 J Wiley, New York (1955)

(15) H PESSEN, *Science* **134**, 676 (1961)

(16) F BASOLO, J CHATT, H B GRAY, R G PEARSON and B L SHAW, *J Chem Soc* 2207 (1961)

TABLE 1 – ORDER IN REACTANT MOLECULES

Phosphonitrile	*m*	*n*
$N_3P_3F_6$	0 68–1 15	0 62–1 30
$N_4P_4F_8$	0 86–1 09	0 68 1 19
$N_3P_3Cl_6$	0 72–1 21	0 73 1 38
$N_4P_4Cl_8$	0 67–1 20	0 65 1 17
$N_3P_3Br_6$	0 77 1 25	0 80 1 25
$N_4P_4Br_8$	0 68 1 20	0 70–1 25

TABLE 2 – PESSEN METHOD OF ANALYSIS

Phosphonitrile	V	k_2 (min^{-1}mole^{-1} l)	Reaction completed in first 10 min * (%)
$N_3P_3F_6$	2 14	25 300	15
$N_4P_4F_8$	2 24	200–1,000	26
$N_3P_3Cl_6$	2 10	2 000 6,700	36
$N_4P_4Cl_8$	2 20	8,000 10,000	40
$N_3P_3Br_6$	2 00	20,000 80,000	38
$N_4P_4Br_8$	2 22	20,000 160 000	68

* $(NPX_2)_n$ RNH$_2$ 1 12 for $n = 3$, 1 16 for $n = 4$ All at 10^{-4} M

TABLE 3 – DATA FROM HALF-LIFE* AND PSEUDO k_1' CALCULATION

Phosphonitrile	k_2 (min^{-1}mole^{-1} l)	k_1' min^{-1}	k_2' (min^{-1}mole^{-1} l)
$N_3P_3F_6$	17–300	0 035–0 050	35–500
$N_4P_4F_8$	133–1 880	0 041–0 037	41–366
$N_3P_3Cl_6$	1,300 6 600	0 070–0 152	152–700
$N_4P_4Cl_8$	3 000–6,670	0 129–0 246	246–1 290
$N_3P_3Br_6$	2,400–20 000	0 085–0 220	220–850
$N_4P_4Br_8$	20 000–180 000	0 195 0 274	195–2,740

* $k_2 \quad 1/at\frac{1}{2}$

Although the rate-determining step is indicated to be second order in all instances, simultaneous fast first-order processes may not be excluded from mechanistic considerations since DOSTROVSKY and HOLMANN(17) have shown that an amino substituent on a phosphorus atom enhances the loss of halogen from that atom by an S_N1 process It is essential, of course, to extend these investigations to other solvents to determine whether the S_N2 rate constants change and thus to establish whether or not a more complex rate-determining step involving interaction with the solvent exists In that successive aminolysis reactions are occurring, only the slowest step is being detected A complete interpretation of mechanism will require evaluation of rates of aminolysis of the partially substituted derivatives, $N_3P_3(NHR)_{6-n}X_n$ A promising beginning has been made by SHAW (10)

The minimal reactivity of the trimeric fluoride suggests the least availability of *d*-orbitals from the phosphorus atoms for nucleophilic attack with this compound A higher degree of aromaticity for this compound through involvement of the phosphorus *d* orbitals with the nitrogen *p*-orbitals in d_π p_π ring interaction would reduce orbital availability. That the trimeric chloride reacts completely with trimethylamine whereas the trimeric fluoride undergoes no reaction(18) supports the concept of greater resonance stability in the latter compound and greater availability of *d*-orbitals for SN_2 attack in the former.

---

(17) I DOSTROVSKY and M HOLMANN, *J Chem Soc* 502 (1953)

Data for the aminolysis of the phosphorohalidates ($R_2POF < R_2POCl < R_2POI$) show the same trend in halide reactivity, however.(17) Since no ring resonance can be involved with these compounds, it is reasonable to assume that the steric environment of the phosphorus atom may also influence the reactivity of substituted groups. If the formation of a transition-state intermediate with penta-substituted phosphorus is required, the greatest difficulty in its formation should be noted with the most rigid planar ring, i.e. that of the trimeric fluoride. The less rigorous conformational requirements about phosphorus in the trimeric chloride and bromide might then allow the formation of a transition-state intermediate with less difficulty. The greater reactivity of the less rigidly structured tetramers may be a consequence of the same general situation since greater steric flexibility about a phosphorus atom more readily allows the conformational changes required in the formation of intermediates. The data cited above do not agree with the suggestion that the bulk effects of the amine(9) are of primary importance in accounting for a greater rate of aminolysis with the tetrameric chloride than with the trimeric chloride.

The polarizability of the halogen atom being replaced will also influence the over-all rate of substitution, other factors being equal. This would suggest the order $I > Br > Cl$.

It is apparent from these preliminary observations that extensive kinetic investigations will be necessary before the solvolytic reactivities of the phosphonitrilic halides can be completely understood. That reactions of this type proceed at measurable rates should be helpful in studies of this type.

Acknowledgement—Support received by S. G. K. from the Ethyl Corporation and E. I. du Pont de Nemours and Company in the form of graduate fellowships is gratefully acknowledged.

---

(18) A. B. BURG and A. P. CARRON *J. Amer. Chem. Soc.* **81**, 836 (1959).

J Inorg Nucl Chem 1963 Vol 25 pp 1401 to 1408 Pergamon Press Ltd Printed in Northern Ireland

THE FORMATION OF COBALTIC ACETATE IN THE CATALYTIC DECOMPOSITION OF PEROXYACETIC ACID

E KOUBEK and J O EDWARDS
Metcalf Research Laboratory, Brown University, Providence 12 R I

(*Received* 25 *March* 1963)

Abstract The kinetics and mechanism for the decomposition of peroxyacetic acid by cobaltous acetate have been investigated The reaction is first order in peroxyacetic acid and varies from one to one-half order in cobaltous acetate depending on its initial concentration During the decomposition reaction "cobaltic acetate" is formed This compound has been isolated and investigated Evidence is presented which indicates that the compound is

$[(Ac)_2CO(OH)_2CO(Ac)_2]$ in which acetate ion is serving as a chelating ligand

SEVERAL workers have reported the preparation of a compound which has been loosely referred to as "cobaltic acetate"(1 5) The method of preparation employed(1 4) involved the electrolytic oxidation of a cobaltous acetate solution in glacial acetic acid to which small amounts of water had been added Although the same product appears to have been isolated by all these groups of workers, there is considerable disagreement as to its structure and even as to its composition SCHALL and co-workers(1,2) claim to have prepared the compound $Co(Ac)_3$ or $Co_3(Ac)_9$ while KYUNO and SHIBATA(4) suggest that the cobalt in their compound is present in the form of the dimeric cation, $[(HAc)_4Co(OH)_2Co(HAc)_4]^{4}$ SHARP and WHITE(3) appear to have investigated their product in greater detail, however they were unable to arrive at any definite conclusions as to its structure or composition As a result of conflicting experimental evidence, they suggest that the green solid isolated from the electrolytic process may actually be a mixture instead of a single compound PESCHANSKI and WORMSER(5) claim to have obtained a series of compounds corresponding to definite formulas such as $Co[(Ac)_3(H_2O)Co(OH)_2Co(H_2O)(Ac)_2]$ and $Co[(Ac)_3Co(OH)_2Co(OH)(Ac)_2]$ while oxidizing solutions of cobaltous salts with alkaline persulphate in the presence of acetate ion However, these structures were apparently deduced simply from elemental analysis and from the ratio of cobalt (III) to total cobalt, which in most cases was reported to equal $\frac{2}{3}$ It is of interest to note that divalent cobalt has been assigned the role of a cation instead of considering the crude product a mixture as was done by SHARP and WHITE However, it is surprising that the cobaltous ions are not shown to be hydrated If they are assumed to be hydrated there would appear serious discrepancies between the compositions calculated on the bases of the proposed structures and those found experimentally

---

(1) C SCHALL and H MARKGRAF, *Trans Amer Electrochem Soc* **45,** 161 (1924)

(2) C SCHALL and C THIEME-WIEDTMARCKTER, *Z Elektrochem* **35,** 337 (1929)

(3) J A SHARP and A G WHITE, *J Chem Soc* 110 (1952)

(4) M F KYUNO and M SHIBATA, *Nippon Kwagu Kwai Shi* **77,** 1434 (1956)

(5) D PESCHANSKI and Y WORMSER, *C R Acad Sci Paris* **252,** 1607 (1961)

It has been found now that oxidation of a solution of cobaltous acetate with peroxyacetic acid gives a green material which the experimental evidence suggests is the compound shown in Fig 1 The catalytic decomposition of peroxyacetic acid, which occurs during the formation of the cobaltic complex, has also been investigated The kinetics of decomposition were found to be in agreement with the proposed dimeric nature of the complex Possible mechanisms for the decomposition of peroxyacetic acid are discussed

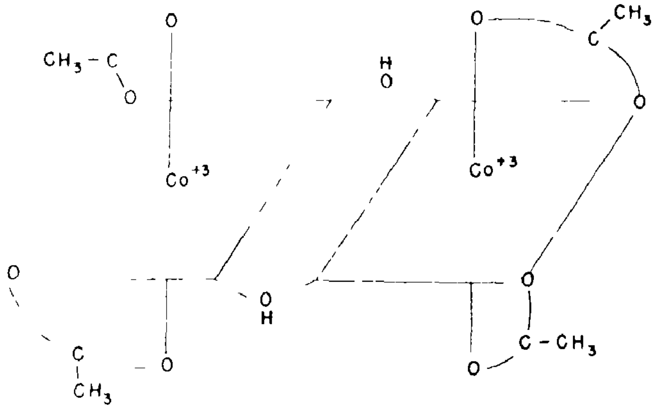


FIG 1

EXPERIMENTAL

Preparation of the cobaltic complex Five millilitres of a concentrated (~708 per cent) solution of peroxyacetic acid were slowly added to 20 ml of an ice-cold saturated solution of cobaltous acetate (Caution this reaction is extremely exothermic and is accompanied by vigorous gas evolution Concentrated peroxyacetic acid should not be allowed to come into contact with a cobalt-containing solid) After the addition of peroxyacetic acid, the reaction mixture was allowed to stand until the evolution of gas had ceased The solution was then immediately placed in a desiccator over sulphuric acid, evacuated and allowed to evaporate to dryness The resulting product was a green amorphous solid which could not be recrystallized

Analytical methods Elemental analysis of the green solid was carried out by the Schwarzkopf Microanalytical Laboratory, Woodside, N Y The percentage of total cobalt present as Co (III) was determined as follows A known weight of the solid was added to a 1 M sulphuric acid solution containing a known excess of standard ferrous sulphate After standing under nitrogen until the initial green colour disappeared (roughly 5 min), the solution was back-titrated with standard ceric solution to an orthophenanthroline endpoint The total cobalt content of the sample was determined by a standard volumetric method (6)

Basic titration curves were obtained with the aid of a Beckman Model G pH meter

Spectroscopy Absorption spectra were determined with a Cary model 14 recording spectrophotometer Solution spectra were recorded using 1 or 5 cm matched quartz cells while the spectra of solids were obtained upon samples mounted in pressed potassium bromide disks Gas samples were studied in conventional 10 cm cells with sodium chloride windows

Molecular weight determinations These measurements were made with a Beckman thermometer in glacial acetic acid by the usual freezing point depression method using a cryoscopic constant of 3 90.(7)

Gas analyses A quantitative measure of the amount of carbon dioxide liberated by the catalytic decomposition was accomplished by absorption of the gas into a solution of barium hydroxide and then determining the precipitated barium carbonate gravimetrically Infra-red measurements of sample of the gas which remained after absorption confirmed the efficiency of the method Mass spectral analyses were performed at Bell Telephone Laboratory, Murray Hill, N J Extreme care was exercised throughout to exclude all atmospheric gases

---

(6) W W Scott, *Standard Methods of Analysis*, p 318, Van Nostrand, New York (1939)

(7) *Handbook of Chemistry and Physics*, p 1956 Chemical Rubber Publishing Co , Cleveland, Oh (1952)

Preparation of labelled peroxyacetic acid Peroxyacetic acid, doubly labelled with oxygen eighteen, was prepared starting from doubly labelled oxygen gas obtained from the YEDA Research and Development Co , Rehovoth, Israel The doubly labelled oxygen gas was reacted with metallic sodium to form sodium peroxide which was in turn hydrolysed to hydrogen peroxide This solution was further concentrated with 98 per cent hydrogen peroxide of normal isotopic composition By oxidation of a portion of this peroxide solution with ceric ion (a process which is known not to sever the peroxide bond[8]), the final content of doubly labelled peroxide was found to be 4 per cent The peroxyacetic acid prepared from this hydrogen peroxide was assumed to have the same isotopic composition[9]

Kinetic measurements All runs were carried out in ammonium acetate buffer solutions prepared by passage of ammonia gas into a solution of freshly distilled acetic acid in deionized water The cobalt salt as well as the salts of other transition metals studied (acetates where possible) were recrystallized three times from deionized water before use Constant temperature was maintained throughout each kinetic run by means of a temperature controlled water bath The peroxyacid concentrations were determined iodometrically

RESULTS AND DISCUSSION

Formation of cobaltic acetate At the pH values of the acetate buffers used (4 5–5 8) the spontaneous decomposition[10] and hydrolysis of peroxyacetic acid was found to be negligible In the presence of exceedingly small amounts of ionic cobalt, rapid decomposition was observed Subsequent experiments showed cobalt salts to be more than 200 times as effective as equivalent amounts of Mn (II) ion, the second most effective catalytic ion Of lesser activity were Fe (III) Cu (II), UO_2 (II) and Cr (III) ions in that order Ions showing no catalytic effect were Pb (II), Tl (I) and Ni (II) Since extreme care was taken to exclude extraneous metal ions any promotional effects are believed to be negligible Due to its greater activity, the cobalt catalysed decomposition was studied in detail

The decomposition in solutions of varying cobaltous acetate concentrations (10^{-3} 10^{-6} M) was found to be first order in peroxyacid concentration, i e log (peroxyacid) vs time gave linear plots to 90 per cent reaction A plot of the log of the observed first order rate constant vs the log of the initial cobalt concentration varies in slope changing from 1 at 10^{-6} M cobalt to ½ at 10^{-3} M cobalt (Fig 2) The order in hydroxide ion varies slightly in the pH range 4 5–5 8, being approximately 0 2 The rate of decomposition also increases with temperature the activation energy amounting to 21 6 ± 1 kcal/mole However, at a constant pH and temperature the experimentally observed rate law for the reaction is

$$\text{Rate} = \frac{k[\mathrm{CH_3CO_3H}][\mathrm{Co}]_0}{k_1 + [\mathrm{Co}]_0^{\frac{1}{2}}}$$

This may easily be explained in terms of a cobalt monomer-dimer equilibrium i e , $2\,M \overset{k}{\rightleftharpoons} D$, with only the monomeric species being catalytically active

The reaction solutions which contained from 10^{-4} to 10^{-3} M cobaltous ion initially were found to turn green immediately upon the addition of peroxyacetic acid The

[8] A F Cahill and H Taube, *J Amer Chem Soc* **74**, 2312 (1952)

[9] C A Bunton, T A Lewis and D R Llewellyn *J Chem Soc* 1226 (1956)

[10] F Koubek, M L Haggett C J Battaglia K M Ibne-Rasa H Y Pyun and J O Edwards, *J Amer Chem Soc* **85**, 2263 (1963)

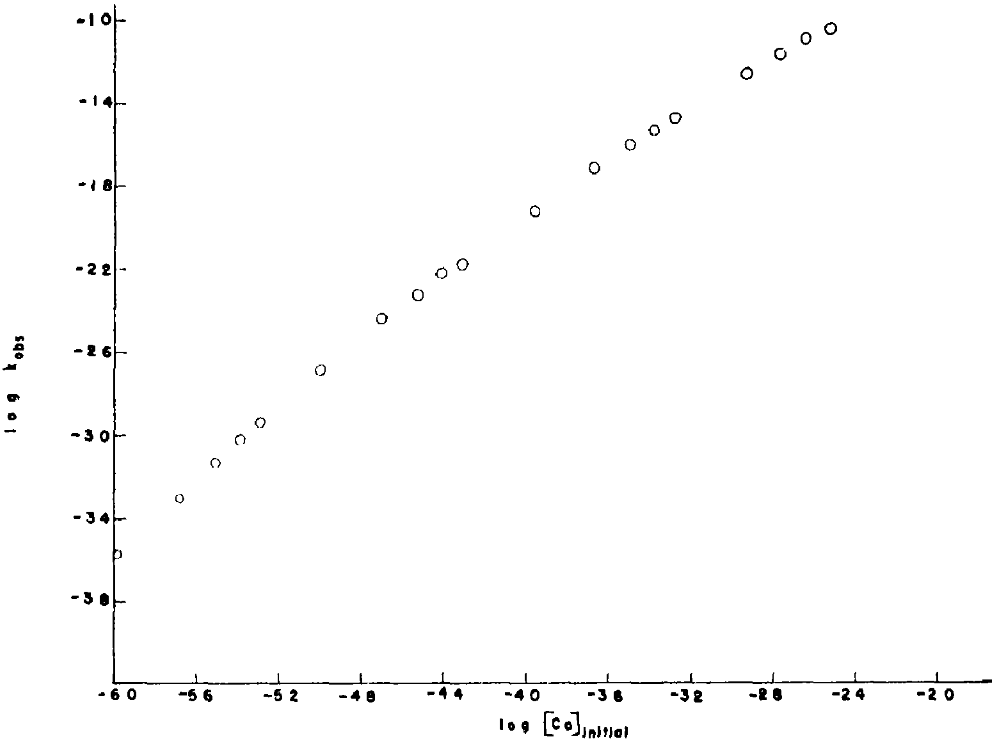


FIG. 2. Log of the observed first order rate constant in lit per mole-min vs the log of the initial concentration of cobaltous acetate for the cobalt catalysed decomposition of peroxyacetic acid. pH 5.4. Temp 19.9°.

ultra-violet and visible absorption spectra of these solutions correspond to those reported for "cobaltic acetate",(3,4) i.e., an absorption maximum at 610 mμ with $\epsilon_{max} \simeq 121$ and a band at 360 mμ with $\epsilon_{max} \simeq 922$. This second band does not reach a maximum even at the limit of the measurements, 210 mμ. Spectral analyses of the solutions made from the solid green cobalt complex isolated show them to have identical absorption spectra as the above mentioned reaction solutions. The solid complex dispersed in a potassium bromide disk also has an identical absorption pattern. Thus, it is believed that the green complex isolated and investigated in detail is actually the same as the one present in solution during the decomposition of peroxyacetic acid, although it, itself, appears to be catalytically inactive.

Further evidence that the green complex, which is presumably the dimer, is catalytically inactive is suggested by the fact that addition of EDTA to the reaction mixtures at any point stops the decomposition reaction immediately. However, the color of the green complex persists for several minutes, slowly changing to a deep red characteristic of the EDTA cobaltic (III) ion complex.(11) Therefore the green complex which persists even in the absence of decomposition cannot itself be catalytically active.

Samples of the green complex isolated were analysed and found to contain up to 90 per cent of the total cobalt in the trivalent oxidation state. At times the cobalt (III) concentration was as low as 66 per cent of the total cobalt content corresponding to the work of PESCHANSKI and WORMSER.(5) However, PESCHANSKI and WORMSER also

(11) M. MORI, M. SHIBATA, E. KYUNO and H. NAKAJUMA, *Bull. Chem. Soc. Japan* 29, 887 (1956).

claimed to have isolated samples of higher Co (III) content and, in these, postulated the compound $Na_4[(Ac)_3(OH)Co(OH)_2Co(OH)(Ac)_3]$ in addition to those previously mentioned. All attempts to remove the small amounts of cobaltous ion present proved unsuccessful. Unfortunately, no solvent or mixture of solvents could be found for recrystallization. The ion-exchange methods suggested by SHARP and WHITE[(3)] gave non-reproducible results which are probably due to decomposition of the compound as well as the resin. In view of the difficulties originally encountered by SHARP and WHITE, this procedure was not investigated further.

Nevertheless, the results of the elemental analysis of a sample containing 86 per cent total cobalt as Co (III) are as follows:

Element	Calculated (%)	Found (%)
Carbon	24.7	23.8
Cobalt	30.4	31.5
Hydrogen	3.6	4.0
Oxygen	41.3	40.6 (by difference)

The calculated values correspond to the compound shown in Fig. 1. The infra-red spectrum of the solid is essentially that of cobaltous acetate, except for a very sharp O—H absorption. No absorption is present in the region of 1000–700 cm^{-1} confirming the absence of a peroxidic group. Therefore, even though the above results were obtained upon an impure, cobaltous containing solid, the impurity was apparently cobaltous acetate and as such would have introduced very little error into the above results.

The molecular weight of the green solid determined by the freezing point depression of glacial acetic acid was found to be 378–388 g/mole which is in excellent agreement with the theoretical value 387.96. No apparent decomposition of the complex was observed in glacial acetic acid at room temperature during the course of these measurements.

That the green compound does in fact contain two hydroxy-bridges is supported by the basic titration experiments. These show that two moles of hydroxide ion are necessary to precipitate one mole of cobalt as $Co(OH)_3$ from the original green complex. That one mole of OH$^-$ present exists as a bridging ion is strongly suggested by the following set of experiments conducted with the chelating agent nitrilotriacetate $N(CH_2CO_2H)_3$ = ata.

It has been shown by MORI *et al.*[(12)] that this compound (ata) acts as a quadridentate ligand toward cobaltic ion forming several types of compounds. The two of main interest here are the monomeric $[Co\ ata(OH)(H_2O)]^-$ and the dimeric $[ata\ Co(OH)_2Co\ ata]^{2-}$. Both compounds have been fairly well established and their absorption spectra reported.[(12)]

It was found in this laboratory that if peroxyacetic acid was added to a buffered cobaltous acetate solution containing nitrilotriacetate, a deep violet colour appeared immediately. By means of the absorption spectrum it was found that the cobaltic ion formed was present as the monomeric [Co ata(OH)(H_2O)]⁻ ion. The catalytic activity of this complex was found to be negligible. However, if the chelate was added to an actually decomposing peroxyacetic acid solution, i.e., one in which peroxyacetic acid and the usual green complex were present, decomposition immediately stopped. The green colour still remained for several minutes (again indicating that the green complex by itself cannot be an active catalyst) but then turned to a pale blue which lasted much longer, and finally the solution became a dark violet. Examination of the absorption spectra during the course of these colour changes clearly indicated that the original green complex gave way to the dimeric nitrilotriacetate complex [ata Co(OH)$_2$Co ata]$^{2-}$ which was in turn slowly transformed into the apparently more stable monomeric form [Co ata(OH)(H_2O)]⁻. As a result of these observations it seems reasonable to assume that the intermediate hydroxy-bridged nitrilotriacetate cobaltic complex results from replacement of acetate groups of the original hydroxy-bridged green complex by two nitrilotriacetate groups. This is then followed by rupture of the bridging bonds to give two monomers. If the original green complex did not contain two hydroxy-bridging groups it is difficult to understand why the intermediate formation of the dimeric species [ata Co(OH)$_2$Co ata]$^{2-}$, should be observed.

---

(12) M. MORI, M. SHIBATA, E. KYUNO and Y. OKUBO, *Bull. Chem. Soc. Japan* **31**, 940 (1958).

However, although much of the evidence strongly supports such a structure as given in Fig. 1, there are some objections which must also be pointed out. These arise from the fact that acetate ion seldom serves as a bidentate ligand. Acetate ion may serve as a bridging ligand in complexes such as [AcH$_2$OCu(Ac)$_2$CuH$_2$OAc](13) and as a chelating ligand in Na[UO$_2$(Ac)$_3$](14) but in these compounds a more favored geometric arrangement is involved than is required for [(Ac)$_3$Co(OH)$_2$(Ac)$_3$].

Decomposition of peroxyacetic acid. Mass spectral and infra-red analyses of the gas evolved during this decomposition revealed the presence of only three compounds, carbon dioxide, carbon monoxide and oxygen. The major portion of the gas consisted of oxygen and carbon dioxide in roughly a 1 : 1 ratio while the carbon monoxide present amounted to only 3–4 per cent (See Table 1A). This is contrary to the results reported by VRBASKI and BRIHTA(15) who claim that the products of the cobalt catalysed

TABLE 1A – PER CENT COMPOSITION OF THE GAS EVOLVED DURING THE COBALT CATALYSED DECOMPOSITION OF PEROXYACETIC ACID

Sample	Hydrogen	Nitrogen	Oxygen	Carbon Dioxide	Carbon Monoxide	Water
I	0.03	0.00	44.83	38.03	3.64	13.44
II	0.00	1.27	46.20	47.30	3.18	2.13

---

(13) F. A. COTTON and G. WILKINSON, *Advanced Inorganic Chemistry*, p. 756. Interscience, New York (1962).

(14) F. A. COTTON and G. WILKINSON, *Advanced Inorganic Chemistry*, p. 901. Interscience, New York (1962).

(15) T. VRBASKI and T. BRIHTA, *Arhiv za Kemiju* **26**, 267 (1954).

is assumed that the alkali chloride activity can be calculated in the manner of Temkin(7)

$$a_{\mathrm{MCl}} = (X_{\mathrm{M}}/X_{\mathrm{cation}})(X_{\mathrm{Cl}}/X_{\mathrm{anion}}) \tag{3}$$

and if CrCl_n^{3-} is the principal Cr containing ion, the nominal X_{CrCl_n} required to lower the MCl freezing point from T_0 to T is*

$$\ln[a_{\mathrm{MCl}}] = \ln[(1-4X_{\mathrm{CrCl}_n})/(1-3X_{\mathrm{CrCl}_n})]$$
$$= \left[-\Delta H_f(T^{-1}-T_0^{-1}) - \int_{T_0}^{T} T^{-2}\int_{T_0}^{T}\Delta C_p\, dT\, dT\right]/R \tag{4}$$

The predicted melting points of the experimental MCl-CrCl$_3$ mixtures were calculated from Equation (4). These temperatures are plotted in the form

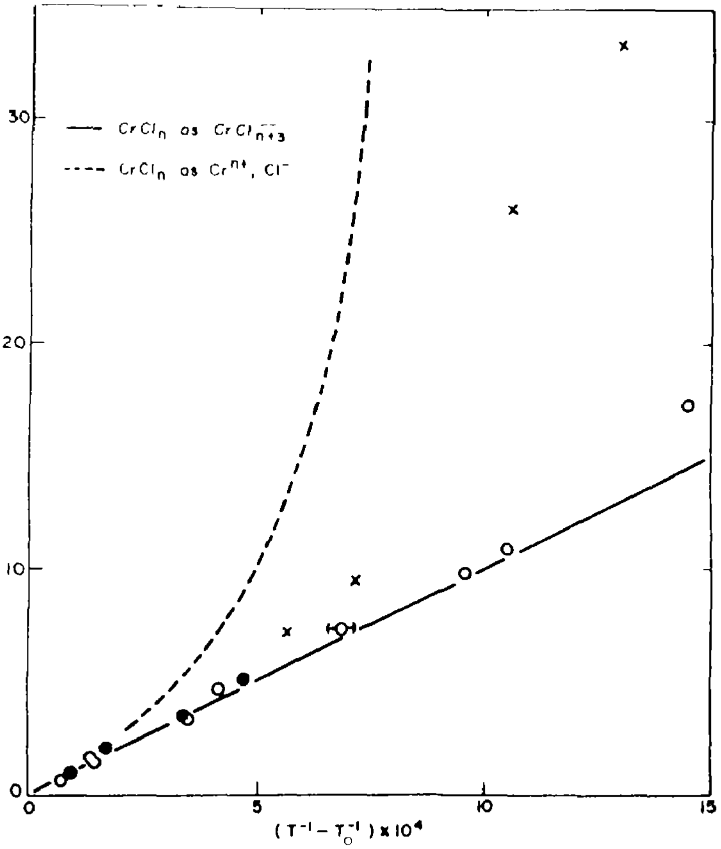


Fig 4—Comparison of calculated vs observed MCl m p for ○ CrCl$_3$ in NaCl, ● CrCl$_3$ in KCl, CrCl$_2$ in NaCl

The Function $f(X,T) = \left[R\ln(1-4X_{\mathrm{CrCl}_n})/(1-3X_{\mathrm{CrCl}_n}) - \int_{T_0}^{T} T^{-2}\int_{T_0}^{T}\Delta C_p\, dT\, dT\right]/\Delta H_f$

---

* In the calculation of $f(X,T)$ of Fig 4 the values ΔH_f (NaCl) = 6690 cal/mole, ΔH_f° (KCl) = 6340 cal/mole were from Dworkin and Bredig,(8) The ΔC_p's were from Kelley (9)

(7) M Temkin, *Acta Phys Chem* U R S S **20,** 411 (1945)

(8) A S Dworkin and M S Bredig, *J Phys Chem* **64,** 269 (1960)

(9) K K Kelley U S Bureau of Mines Bulletin 584, (1960)

decomposition of peroxyacetic acid are oxygen and acetic acid. Quantitative determination of the carbon dioxide evolved suggests that the reaction

$$3CH_3CO_3H \xrightarrow{Co} CO_2 + O_2 + 2CH_3CO_2H$$

is taking place. However, it was found that during the decomposition of the peroxyacid, in ammonium acetate buffer containing carbon 14 in the carbonyl position, up to 30 per cent of the carbon dioxide liberated arises from the acetate buffer. Since it has been shown that any exchange between peroxyacetic acid and acetate ion which may occur is slow,[16] one must conclude that the decomposition is taking place, at least in part, *via* a free radical mechanism involving acetate ions of the buffer.

Perhaps even more interesting is the fact that the experiments with doubly labelled peroxyacetic acid show that the peroxide bond remains intact during catalytic decomposition at the higher concentrations of cobalt (~10^{-3} M) (See Table 1B). Although it has also been shown that the peroxide bond is not broken under certain conditions in the catalytic decomposition of hydrogen peroxide[8,17] we believe that this is the first report of such a result involving a peroxyacid.

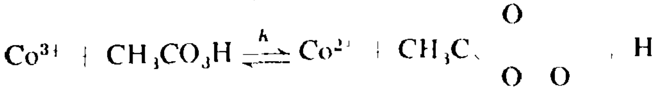
TABLE 1B.—RESULTS OF THE DECOMPOSITION OF SAMPLES ENRICHED WITH DOUBLY LABELLED OXYGEN $^{18}O_2$

Sample	Ratio $^{36}O_2$ + ½ $^{34}O_2$ (total ^{18}O content)
Oxidation of enriched H_2O_2 with excess ceric ion	0.88
Decomposition of enriched peroxyacetic acid prepared from the above H_2O_2 with 10^{-3} M cobaltous acetate	0.86
Decomposition of enriched peroxyacetic acid prepared from the above H_2O_2 with 10^{-4} M cobaltous acetate	0.65

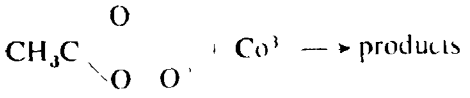
In view of the above observations it is possible that the predominant steps leading to the catalytic decomposition of peroxyacetic acid are as follows

$$CH_3CO_3H + Co^{2+} \xrightarrow{fast} Co^{3+} + CH_3CO_2^{-} + OH \qquad (1)$$

$$2Co^{3+} \overset{k}{\rightleftharpoons} Co_2^{6+} \qquad (2)$$



$$Co^{3+} + CH_3CO_3H \overset{k}{\rightleftharpoons} Co^{2+} + CH_3C(=O)O{-}O^{\cdot} + H^{+} \qquad (3)$$



$$CH_3C(=O)O{-}O^{\cdot} + Co^{3+} \longrightarrow \text{products} \qquad (4)$$

---

[16] G. LEVEY, D. R. CAMPBELL, J. O. EDWARDS and J. MACLACHLAN, *J. Amer. Chem. Soc.* **79**, 1797 (1957).

[17] R. C. JARNAGIN and J. H. WANG, *J. Amer. Chem. Soc.* **80**, 786 (1958).

However, at lower concentrations of Co(II) (~10^{-4} M) significant scrambling (30 per cent) did occur. Presumably at this concentration reaction (4) is beginning to be replaced by a step such as

$$2CH_3CO_3 \longrightarrow O_2 + \text{products} \qquad (5)$$

A similar situation(18,19,20) is believed to exist in the case of the oxidation of hydrogen peroxide by varying amounts of Ce(IV). Although the scheme given above is consistent with the kinetic behaviour, the products obtained and the labelling experiments, it is by no means meant to be all inclusive.

Acknowledgement—The authors wish to express their appreciation to the U.S. Atomic Energy Commission for its financial assistance and to Dr. M. J. HAGGETT for many helpful discussions.

(18) G. CZAPSKI, B. H. J. BIELSKI and N. SUTIN, *J. Phys. Chem.* **67**, 201 (1963).
(19) B. H. J. BIELSKI and E. SAITO, *J. Phys. Chem.* **66**, 2266 (1962).
(20) W. T. DIXON and R. O. C. NORMAN, *Nature, Lond.* **196**, No. 4857, 891 (1962).

J. Inorg. Nucl. Chem. 1963. Vol. 25, pp. 1409 to 1413. Pergamon Press Ltd. Printed in Northern Ireland

THE PREPARATION OF METAL-β-KETOIMINE COMPOUNDS BY CHELATE EXCHANGE*

A. W. STRUSS and D. F. MARTIN
W. A. Noyes Laboratories, Department of Chemistry and Chemical Engineering, University of Illinois

(Received 11 April 1963)

Abstract—The scope and limitations of chelate exchange as a method of preparation of metal-β-ketoimine compounds is described. The outstanding advantage of the method is that it minimizes hydrolysis and amine exchange, side-reactions frequently encountered with other methods. The main disadvantage of chelate exchange as a synthetic method is the requirement of a favourable equilibrium.

In connection with studies of the reactions involving metal ions and β-keto-imines,(1–4) it has been noted that hydrolysis is an interference. Another side reaction, amine exchange, has been reported.(2) It seems reasonable to believe that chelate exchange, $MCh_n + n\,HCh' \rightarrow MCh_n' + n\,HCh$, which is displacement of a chelate from the co-ordination sphere of a metal ion by another chelate, might be less subject to these side reactions and would be a useful preparative method.

The preparation of β-ketoimine–metal compounds by chelate exchange seems never to have been reported. However, chelate exchange has been used to prepare co-ordination polymers (e.g., by reaction of a metal acetylacetonate and a bis-(β-diketone),(5) copper(II) derivatives of salicylaldimines and β-diketones(6) and "mixed" β-dicarbonyl compounds, Cu(RCOCHCOR′)(R″COCHCOR‴).(7)

EXPERIMENTAL†

Preparation of ligands and metal–chelate compounds. Unless otherwise noted, the preparation and properties of the ligands and metal–chelate compounds are described elsewhere.(1–3) *Bis(1-phenyl-3-iminobutane-1-ono)*copper(II) was prepared according to the directions given by HOLTZCLAW and coworkers.(8) The ligand was purified by recrystallization from 95 per cent ethanol (65 per cent yield, m.p. 141–143°, reported,(8) 143°), and the metal–chelate compound was recrystallized from acetone (nearly quantitative yield), light green crystals, m.p. 188–190°. (Found: C, 62.08; H, 5.29. Calc. for $C_{20}H_{20}O_2N_2Cu$: C, 62.60; H, 5.22%.)

Bis[N-(n-butyl)salicylaldimino]metal(II) compounds. The *copper(II)*(9), *nickel(II)*(9), and *zinc(II)*(10)

---

* Taken in part from the B.S. Thesis of Arthur W. Struss, August 1962, University of Illinois.

† All microanalyses were performed under the direction of Mr. J. NEMETH.

(1) D. F. MARTIN, G. A. JANUSONIS and B. B. MARTIN, *J. Amer. Chem. Soc.* **83**, 73 (1961).
(2) D. F. MARTIN, *Advances in Chem. Ser.* No. 37, 192 (1963).
(3) P. J. MCCARTHY, R. J. HOVEY, K. UENO and A. E. MARTELL, *J. Amer. Chem. Soc.* **77**, 5820 (1955).
(4) J. P. COLLMAN and E. T. KITTLEMAN, *Inorg. Chem.* **1**, 499 (1962).
(5) F. H. HOLST, Doctoral Dissertation, The Pennsylvania State University (1955).
(6) T. MUTO, *Nippon Kagaku Zasshi* **76**, 252 (1955); *Chem. Abstr.* **51**, 17559 (1957).
(7) I. S. MOORE and M. W. YOUNG, *J. Chem. Soc.* 2694 (1932).
(8) H. F. HOLTZCLAW, JR., J. P. COLLMAN and R. M. ALIRE, *J. Amer. Chem. Soc.* **80**, 1100 (1958).
(9) R. G. CHARLES, *J. Org. Chem.* **22**, 677 (1957).
(10) R. G. CHARLES, *J. Inorg. Nucl. Chem.* **9**, 145 (1959).

compounds were prepared as described by CHARLES.[9,10] The observed melting points (79–81°, 138–140°, 151–152°) were in agreement with those reported (80.5–81°, 141.8–142.4°, 152–152.5°). The *cobalt(II)* compound was prepared similarly except that heating was not required and oxygen-free water was used. A nitrogen atmosphere was maintained during the preparation and recrystallization of the compound. In this way, red needles were obtained, m.p. 151–153° (from acetone), 75 per cent yield. (Found: C, 63.61; H, 6.85. Calc. for $C_{22}H_{28}O_2N_2Co$: C, 64.20; H, 6.81%.)

Chelate-exchange reactions. Two general methods were used in attempted chelate-exchange reactions. *Method A* consisted in mixing and heating solutions (alcohol or benzene usually) of a β-ketoimine metal compound and another β-ketoimine. The product was precipitated by addition of water (if alcoholic solutions were used) or petroleum ether (benzene solution). The products were identified by comparison with authentic samples. *Method B* was similar except that the source of the metal was the N-(n-butyl)-salicylaldimine metal compound. In all cases, stoicheiometric amounts of reactants were used.

Preparation of bis-(3-phenylimino-1-phenylbutane-1-ono)copper(II), $[C_6H_5COCHC(=NC_6H_5)-CH_3]_2Cu$. *By chelate exchange.* A solution of bis(4-iminopentane-2-ono)copper(II) (1.3 g, 0.005 mole) and 3-phenylimino-1-phenylbutane-1-one (2.37 g, 0.01 mole), in 75 ml of 95 per cent ethanol was refluxed for 1 hr, during which time a dark precipitate formed. The mixture was cooled in an ice–water bath, and 1.6 g of crystals were collected by filtration. An additional 0.8 g of crystals were obtained by adding water to the hot filtrate until crystals began to form. Recrystallization of the crude material from 95 per cent ethanol afforded 1.73 g (64.5 per cent) of green platelets, m.p. 180–182°. (Found: C, 71.58; H, 5.17; N, 5.30. Calc. for $C_{32}H_{28}O_2N_2Cu$: C, 71.70; H, 5.23; N, 5.23%.)

Attempted preparation by direct synthesis. To a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.25 g, 1 mmole) in 5 ml of 95 per cent ethanol was added five drops of 15 N ammonium hydroxide followed by a warm solution of ligand (0.24 g, 1 mmole) in 10 ml of 95 per cent ethanol. The lustrous green platelets that formed at once were collected (yield ca. 0.3 g) m.p. 174–176°. (Found: C, 63.42; H, 5.31; N, 8.04. Calc. for $[C_6H_5COCHC(=NH)CH_3]_2Cu$: C, 62.48; H, 5.25; N, 7.33%.) This compound differs slightly in colour and melting point from an authentic sample (prepared by the method of HOLTZCLAW[8]). However, the infra-red absorption spectra (Nujol-hexachlorobutadiene mulls) are identical.

Isolation of a "mixed" metal–chelate compound. A solution of bis(4-iminopentane-2-ono)copper(II) (1.3 g, 0.005 mole) and 4-phenyliminopentane-2-one (1.75 g, 0.01 mole) in 50 ml of methanol was refluxed for 2 hr. Water was added to the hot mixture to initiate crystallization, the mixture was allowed to cool, and gray needles, 1.5 g (89.5 per cent), m.p. 90–91°, were collected by filtration. (Found: C, 55.95; H, 5.99; N, 7.96. Calc. for $[CH_3COCHC(=NH)CH_3][CH_3C(=NC_6H_5)CH-COCH_3]Cu$: C, 57.30; H, 5.96; N, 8.35%.) A solution of "mixed" chelate (1.5 g, 0.0057 mole) and 4-phenyliminopentane-2-one (1.0 g, 0.0057 mole) in 30 ml of 95 per cent ethanol was refluxed for 2 hr. Water was added to the hot solution to initiate crystallization, 0.8 g (43 per cent) of brown platelets, m.p. 131–133°, were obtained by filtration. (Found: C, 63.61; H, 6.06; N, 7.10. Calc. for $[CH_3C(=NC_6H_5)CHCOCH_3]_2Cu$: C, 64.08; H, 5.83; N, 6.80%.)

DISCUSSION

The results of attempts to effect chelate exchange are listed in Table 1. For convenience and to indicate the scope of the reaction, the results have been arranged in four sections according to the structure of the reactant and product.*

There are four advantages in the use of chelate exchange as a means of preparing metal–β-ketoimine compounds: (1) side reactions are avoided, (2) contamination of the product by extraneous ions is minimized, (3) the operations are facile, and (4) it is possible to prepare "mixed" complexes of the type MChCh′. There are two disadvantages: (1) the exchange equilibrium may be unfavourable, and (2) a less serious objection, the method requires an additional, though readily prepared, metal–chelate

---

* A "monocyclic" metal chelate compound is formed from a bidentate chelate and a metal ion; a "tricyclic" metal–chelate compound is formed from a quadridentate ligand and a metal ion.

TABLE 1—PREPARATION OF COMPOUNDS OF THE TYPE $[RCOCHC(=NR')R'']_2M$ BY CHELATE EXCHANGE

Method[a]	R	R′	R″	M	Solvent[b]	Reaction Time (hr)	Reaction Yield (%)
I Monocyclic → Monocyclic(10)							
A	C_6H_5	C_6H_5	CH_3	Cu	1	1	64.5
A	CH_3	$4\text{-}C_6H_4NO_2$	CH_3	Cu	1	0.5	52
A	CH_3	$4\text{-}C_2H_4NO_2$	CH_3	Ni	2	24	0
A	CH_3	CH_3	CH_3	Cu	1	2	0
A	CH_3	C_6H_5	CH_3	Cu	1	2	42
A	CH_3	C_6H_5	CH_3	Ni	3	3	0
A[c]	CH_3	$2,6\text{-}(CH_3)_2C_6H_3$	CH_3	Ni	4	3	
A	C_6H_5	C_6H_5	CH_3	Ni	2 or 3	15	0
A[c]	C_6H_5	C_6H_5	CH_3	Ni	4	3	
A	C_6H_5	H	CH_3	Cu	1	6	68
A	C_6H_5	C_6H_5	C_6H_5	Cu	4	0.5	34
A	C_6H_5	C_6H_5	C_6H_5	Ni	1	0.25	42
B	CH_3	C_6H_5	CH_3	Ni	2	15	0
B	CH_3	C_6H_5	CH_3	Zn	2 or 4	15	0
B	CH_3	$4\text{-}C_6H_4NO_2$	CH_3	Ni	5	15	0
B	CH_3	$4\text{-}C_6H_4NO_2$	CH_3	Zn	5	15	0
B	C_6H_5	H	CH_3	Co	2	2	0
B	C_6H_5	C_6H_5	CH_3	Co	2	2	0
II Monocyclic → Tricyclic(10)							
A	CH_3	$(CH_2CH_2)_{1/2}$	CH_3	Cu	1	2	83
A	CH_3	$(CH_2CH_2)_{1/2}$	CH_3	Ni[d]	1	3	88[d]
A	CH_3	$(CH_2CH_2CH_2)_{1/2}$	CH_3	Cu	1	3	0
A	CH_3	$(CH_2CH_2CH_2)_{1/2}$	CH_3	Ni	3	3.5	0
A	CH_3	$(CH_2CHCH_3)_{1/2}$	CH_3	Cu	1	2	80
A	CH_3	$(CH_2CHCH_3)_{1/2}$	CH_3	Ni	1	5	88
A[f]	CH_3	$(CH_2CH_2)_{1/2}$	CH_3	Cu	1	2	27
B	CH_3	$(CH_2CH_2CH_2)_{1/2}$	CH_3	Cu	1	24	0
B	CH_3	$(CH_2CHCH_3)_{1/2}$	CH_3	Ni	1	5	30.5
B	CH_3	$(CH_2CH_2)_{1/2}$	CH_3	Zn	2	15	0
B	CH_3	$(CH_2CH_2)_{1/2}$	CH_3	Co	2	4	0
III Tricyclic → Tricyclic							
A	CH_3	$(CH_2CH_2)_{1/2}$	CH_3	Cu	1	0.25	75
A	CH_3	$(CH_2CHCH_3)_{1/2}$	CH_3	Cu	1	0.25	86
IV Tricyclic → Monocyclic							
A	CH_3	H	CH_3	Cu	1	0.5	60

---

[a] Method A β-ketoimine-metal compound + β-ketoimine Method B, N-(n-butyl)salicylaldimine-metal compound + β-ketoimine

[b] Solvents 1, 95 per cent ethanol 2, benzene 3 toluene 4 abs ethanol 5 methanol,

[c] Reference (13) 100 per cent excess of ligand used.

[d] M p 139–143° Found, C, 49.55, H, 6.74, Calc for $C_{12}H_{18}O_2N_2Ni$ C, 51.30 H, 6.41%

[e] Starting material $[C_6H_5COCHC(=NH)CH_3]_2Cu$

[f] Starting material $Cu[CH_3COCHC(CH_3)=NCH_2]_2CH_2$

compound as a starting reagent The favourable and unfavourable aspects of chelate exchange deserve a more detailed consideration

The preparation of $[C_6H_5COCHC(=NC_6H_5)CH_3]_2Cu$ represents a good example of the main utility of chelate exchange, the avoidance of side reactions Since the rate of hydrolysis of β-ketoimines is much lower in basic than acidic medium, most direct methods of preparation of metal β-ketoimines involve the addition of base, frequently ammonium hydroxide Although hydrolysis is minimized by the presence of ammonia, amine exchange$^{(2)}$ can occur and apparently does in the attempted preparation

$$2C_6H_5COCH_2C(=NC_6H_5)CH_3 + Cu^{2+} + 2NH_3 \rightarrow$$
$$[C_6H_5COCHC(=NH)CH_3]_2Cu + 2C_6H_5NH_3$$

By contrast, chelate exchange occurs readily and in fairly good yield

It might also be noted that direct synthesis of necessity involves the addition of extraneous anions to the reaction mixture which may cause contamination of the desired product and increase the problem of separating and purifying the product For this reason, co-ordinating anions such as chloride, bromide and iodide are excluded and acetate or nitrate salts are used Even this may not be sufficient For example, under suitable conditions, copper acetate is an oxidizing agent and copper nitrate is a nitrating agent Moreover, if a secondary or tertiary amine, such as pyridine, is used to prevent hydrolysis and preclude amine exchange, the possibility of contamination remains Pyridine reacts with nickel acetylacetonate,$^{(11)}$ and there is reason to believe that the same is true of certain nickel(II)/β-ketoimine compounds$^{(12)}$ By contrast there are appreciably fewer species present in a chelate exchange process, and the main contaminant is the weakly chelating agent which is formed

The most serious limitation of chelate exchange as a synthetic method is the requirement of a favourable equilibrium For example, the tricyclic compound bisacetylacetonetrimethylenediiminocopper(II), could not be prepared by means of chelate exchange

(monocyclic → tricyclic) –

$$Cu[CH_3COCHC(=NH)CH_3]_2 + [CH_3COCH_2C(CH_3)=NCH_2]_2CH_2 \rightarrow$$
$$Cu[CH_3COCHC(CH_3)=NCH_2]_2CH_2 + 2CH_3COCH_2C(=NH)CH$$

This was surprising since the tricyclic compound was presumed to be more stabl However, the reverse reaction (tricyclic → monocyclic) occurs readily That this i not due to the greater insolubility of bis(4-iminopentane-2-ono)copper(II) is con- firmed by qualitative measurements of the solubility of the two metal chelate com- pounds under condition used for isolation (50 volume per cent ethanol-water and 0 °C) the solubility of the tricyclic compound is about 2×10^{-2} mole l^{-1}, that of the mon cyclic compound is 10×10^{-2}

There are other examples in which solubility rather than stability is importa When the product and reactant metal-chelate compounds differ but little in stabili it may be expected that exchange will not occur unless governed by solubility or th an intermediate, MChCh′, will be formed An example of the latter behaviour is

---

[11] *cf* J P FACKLER, JR , *J Amer Chem Soc* **84,** 24 (1962)

[12] E J OLSZEWSKI, Private communication (1962)

reaction of bis(4-iminopentane-2-ono)copper(II) with 4-phenyliminopentane-2-one In this case, it was possible to isolate the intermediate, [CH$_3$C(=NH)CHCOCH$_3$][CH$_3$C(=NC$_6$H$_5$)CHCOCH$_3$]Cu, and to convert this to the bis(4-phenyliminopentane-2-ono)copper(II) by chelate exchange Thus, chelate exchange appears to offer a synthetic route to "mixed" compounds provided the proper chelates are selected

There are a number of examples of failure of chelate exchange using stoicheiometric amounts of reactants Two approaches have been used in order to overcome these difficulties The first is the use of an excess of ligand, the second, the use of a less stable metal–chelate compound as a reactant The use of excess ligand has been successful in the preparation of [C$_6$H$_5$COCHC(=NC$_6$H$_4$CH$_3$)]$_2$Ni

The use of a higher boiling solvent (toluene for benzene) was not successful, but Hseu has found that the use of a 100 per cent excess of ligand results in the desired compound (13) The use of an excess of ligand introduces a problem of separation, particularly with slightly soluble ligands However this may not be a serious objection since chelate exchange is often the only method that has been found to prepare the desired compounds

Preliminary efforts to prepare cobalt(II) or zinc(II) compounds by chelate exchange have not been successful However, other workers have experienced difficulties in preparing these compounds by direct methods A pure sample of bisacetylacetone-ethylenediiminocobalt(II) has not been prepared(3) though other cobalt(II) salts were prepared The failure to prepare β-ketoimine–zinc(II) compounds by reaction of zinc hydroxide and a β-ketoimine has been reported (14) On the other hand, the preparation of bisacetylacetone-ethylenediiminozinc (II) has been reported, but experimental details were not given (15)

In summary, chelate exchange can be a very useful method for the preparation of copper(II) and nickel(II) β-ketoimine compounds It should be possible to use the general method for the preparation of β-ketoimines of other metals

Acknowledgement This investigation was supported in part by PHS Research Grant 7873 Division of General Medical Sciences U S Public Health Service This is acknowledged with gratitude as is the support provided to one of us (A W S) by a National Science Foundation Undergraduate Participation Program grant

---

(13) T M Hseu, D F Martin and T Moeller *Inorg Chem* **2** 587 (1963)

(14) R J Hovey, J J O'Connell and A E Martell *J Amer Chem Soc* **81**, 3189 (1959)

(15) I Leventhal and C S Garner *J Amer Chem Soc* **71**, 371 (1949)

J Inorg Nucl Chem 1963, Vol 25 pp 1415 to 1422 Pergamon Press Ltd Printed in Northern Ireland

THERMAL DECOMPOSITION OF EUROPIUM(III) OXALATE

A Glasner, E Levy and M Steinberg
Department of Inorganic and Analytical Chemistry, Hebrew University,
Jerusalem, Israel

(*Received* 22 *February* 1963)

Abstract -It is shown that the first step in the thermal decomposition of europium(III) oxalate leads to reduction to the divalent state In an oxidizing atmosphere the europium is reoxidized and continues decomposing gradually to Eu_2O_3 at 390 In an atmosphere of CO_2, Eu(II) Ox is stabilized at 320 In vacuum, $Eu(II)CO_3$ admixed with carbon (originating in disproportionation of CO) is obtained in the temperature range 360 420

A unified mechanism for the decomposition of oxalates is proposed, in which a trace of carbon monoxide acts as catalytic agent in the reductive decomposition of oxalates of reducible metal ions

EUROPIC oxalate differs in its thermal behaviour from the other light rare earth oxalates,(1 2) because of the reducibility of the europic ion Indeed, it appears that the high proportion of carbon dioxide evolved on heating $Eu(III)_2Ox_3$ in vacuum can be explained only by assuming the reaction

$$Eu_2Ox_3 \rightarrow 2EuOx + 2CO_2 \qquad (1)$$

to have taken place A number of other oxalates, for example silver,(3) nickel(4) ferric(5) and plumbous(6) oxalate are known to behave in a similar fashion the cation being reduced either to the metal or to a lower valence state

The singularity of Eu_2Ox_3 has been noted by earlier workers using the thermogravimetric and differential thermal analysis methods (7 8,9) thus WENDLANDT *et al* observed a high and wide exothermic peak on their DTA curve at about 390° They suggest that this strongly pronounced peak is due to oxidation but are unable to offer any explanation for its presence

The present work proves reaction (1) to be the initial step in the thermal decomposition of Eu_2Ox_3 This step is followed by the decomposition of europous oxalate to the carbonate accompanied by an extensive disproportionation of the evolving carbon monoxide A complication sets in at this stage so that the successive steps of the reaction cannot be clearly defined, divalent europium being reoxidized in air to the tervalent state, and even in vacuum or an inert atmosphere, oxidation by carbon dioxide evolving from the decomposing carbonate, takes place at higher temperatures.

---

(1) A GLASNER and M STEINBERG, *J Inorg Nucl Chem* **16**, 279 (1961)
(2) A GLASNER and M STEINBERG, *J Inorg Nucl Chem* **22**, 39 (1962)
(3) A FINCH, P W M JACOBS and F C TOMPKINS *J Chem Soc* 2053 (1954)
(4) P W M JACOBS and A R TARIQ KURFISHY *Proceedings of the 4th International Symposium on Reactivity of Solids* p 352 Elsevier Amsterdam (1960) *Trans Faraday Soc* **58**, 551 (1962)
(5) J B HOLDEN, Jr, *Diss Abstr*, **23**, 62 (1962)
(6) L L BIRCUMSHAW and I HARRIS, *J Chem Soc* 1637 (1939), 1898 (1948)
(7) W W WENDLANDT *Analyt Chem* **30**, 58 (1958), **31**, 408 (1959)
(8) W W WENDLANDT T D GEORGE and G R HORTON *J Inorg Nucl Chem* **17**, 273 (1961)
(9) L C SHEARS, *Trans Brit Ceram Soc* **61**, 225 (1962)

EXPERIMENTAL

Materials

$Eu_2Ox_3 \cdot 5.8H_2O$ was prepared from the oxide (Lindsay, Code 1013, 99.9% purity) by precipitation with saturated oxalic acid solution from a nitric acid solution (1 N) of the oxide. The precipitate was washed with warm water and kept in an evacuated desiccator over P_2O_5. Double analysis, i.e. ignition at 1000°C in air and titration with standard permanganate, proved the oxalate to have the composition and water content indicated above.

A portion of this preparation was dehydrated by heating in vacuum at 200°C, for 30 min. After condensation of the water vapour in acetone dry-ice cold traps no rise of pressure in the vacuum apparatus was observable and hence no initial decomposition of the oxalate itself had taken place. The dehydrated sample still retained some of its water of crystallization, having the composition $Eu_2Ox_3 \cdot 0.3H_2O$.

Decomposition experiments in atmospheres of air, oxygen, nitrogen or carbon dioxide were performed with hydrated oxalate samples weighing 50–300 mg, in the temperature range 280–420°C. The weighed samples were introduced into a tubular oven which had been heated to the required temperature and through which a constant current of pure gas, dried over anhydrone, was allowed to flow. Each run was continued for 24 hr, this length of time having been found sufficient, as a rule, to obtain a residue of constant weight.

A spot-test with ferric thiocyanate was employed to prove the presence of divalent europium in the residues.[10]

In order to determine the amount of carbonate present in the residues, weighed portions were allowed to react with phosphoric acid, and the evolving carbon dioxide was driven over by a current of pure nitrogen and absorbed in weighed ascarite tubes.

Qualitative information on the content of oxalate and/or carbonate of the residues was also obtained from the infra-red spectra, taken by the KBr method.

The apparatus and methods employed in the study of the thermal decompositions in vacuum have already been described.[1] Dehydrated samples of Eu_2Ox_3 weighing 5–8 mg were used in the temperature range 320–420°C. A few experiments were also carried out at temperatures above 500. That the evolving gases contained only carbon monoxide and carbon dioxide was in some instances ascertained by oxidizing the CO with I_2O_5,[11] when all the gases in the apparatus could be condensed out in a liquid air trap.

RESULTS

(a) *Results in various atmospheres*

The results obtained in various atmospheres are presented in Table 1, which shows the weight of the sample, the loss of weight in percentages after heating for 24 hr the reducing power, the weight per cent of CO_2 in the residue, its colour and the composition of the residue. The last column was deduced by comparing the experimental values in Table 1 with the corresponding calculated values for various intermediary decomposition products recorded in Table 2.

In most experiments the samples were placed in a porcelain boat, in a few instances a platinum boat was used as indicated in the table. It may be seen that results wer fairly reproducible, and were not influenced by the container.

The residues obtained in an inert atmosphere (N_2 or CO_2) reduced ferric iron while the decomposition products formed in air or oxygen did not do so. This te suggests that the former contain europous compounds, but the cause of the decrea

---

[10] M. N. AMBROZHII and E. I. LUCHNIKOVA, *Rare earth elements* p. 203. The Academy of Scienc U.S.S.R. (1959).

[11] M. STEINBERG, A. GLASNER and E. LEVY, *Analyt. Chem.* **34**, 1629 (1962).

$(T_{\text{calc}}$ m p $)^{-1} - T_0^{-1}$ as the ordinate in Fig 4, the abscissa is $(T_{\text{obs}}$ m p $)^{-1} - T_0^{-1}$ Agreement between predicted and observed liquidus temperatures prevails to more than 100° below the pure MCl melting points for both the NaCl– and KCl–$CrCl_3$ systems

Cr^{2+} has less charge density and crystal field stabilization than Cr^{3+} and should form less stable complex ionic species in chloride melts This is indicated in Fig 4 by the NaCl–$CrCl_2$ liquidus data$^{(10)}$ which exhibit substantial negative deviations from ideality without, however, pointing to a specific complex species

(10) J C Shiloff, *J Phys Chem* **64**, 1566 (1960)

Acknowledgements—The author wishes to thank Mr G Gorsuch for experimental assistance and G Teufer for aid in interpretation of the X-ray patterns

TABLE 1 WEIGHT LOSS AND CO_2 CONTENT OF SOLID RESIDUES OBTAINED ON DECOMPOSITION OF $Eu_2Ox_3 \cdot 5.8H_2O$ IN VARIOUS ATMOSPHERES

°C	Atmosphere	Wt of sample (mg)	Wt loss (%)	Residue: Reductivity	Residue: Colour	Residue: CO_2 (%)	Residue: Composition
280	air	149.2	25.2		White	1.9	~$(EuOx)_2O$
320	air	186.5	34.2		White	18.8	$(EuCO_3)_2O$
	O_2	86.5	34.9		White		$(EuCO_3)_2O$
	N_2	68.8	34.3		White		$EuCO_3$
	CO_2	229.9	28.6		Grey		$EuOx$
360	air	64.5	42.0		White	–	$(EuO)_2CO_3$
	N_2	161.8	41.6		White	11.2	$Eu_2O_2CO_3$
	CO_2	71.5	34.3		Light Grey		$EuCO_3$
	CO_2	167.4	34.4		Brown	20.6	$EuCO_3$
390	air (Pt)	29.0	47.9		White	–	Eu_2O_3
	O_2	205.9	46.3		White	1.9	Eu_2O_3
	N_2 (Pt)	34.4	46.4		White		EuO
	N_2	223.7	46.3		White	2.1	EuO
	CO_2	154.1	42.9		Grey	10.9	$Eu_2O_2CO_3$
	CO_2	158.6	42.2		Light Grey	11.5	$Eu_2O_2CO_3$
420	O_2	250.2	46.8		White	0.5	Eu_2O_3
	N_2	292.5	46.9	( )	White	1.1	EuO (?)
	CO_2	178.7	46.8	( )	White	1.1	EuO (?)

TABLE 2 CALCULATED WEIGHT LOSS AND PER CENT OF CO_2 IN RESIDUE FOR PROBABLE INTERMEDIARY PRODUCTS

Composition	Wt loss (%)	CO_2 (%)	Composition	Wt loss (%)	CO_2 (%)
Eu_2Ox_3	15.5	0.0	Eu_2O_3	47.6	0.0
$(EuOx)_2O$	26.2	0.0	2 $EuOx$	28.6	0.0
$Eu_2(CO_3)_3$	28.0	27.3	2 $EuCO_3$	36.9	20.3
$(EuCO_3)_2O$	34.5	20.0	$Eu_2O_2CO_3$	43.5	11.5
$(EuO)_2CO_3$	41.1	11.1	2 EuO	50.0	0.0

in their reducing power with increase of temperature is not clear they may have been oxidized in air after removal from the oven

In an atmosphere of CO_2 at 320° the weight loss (28.6 per cent) corresponds exactly to the formation of Eu(II)Ox

$$Eu_2Ox_3 \rightarrow 2EuOx + 2CO_2 \qquad (1)$$

This conclusion is neatly confirmed by the infra-red spectrum of the residue, where only adsorption bands due to the oxalate ion may be observed (Fig. 1 curve 1)

That (1) is the first step in the thermal decomposition in air also may be concluded from the experiment at 280° The weight loss is nearly equal to that expected for

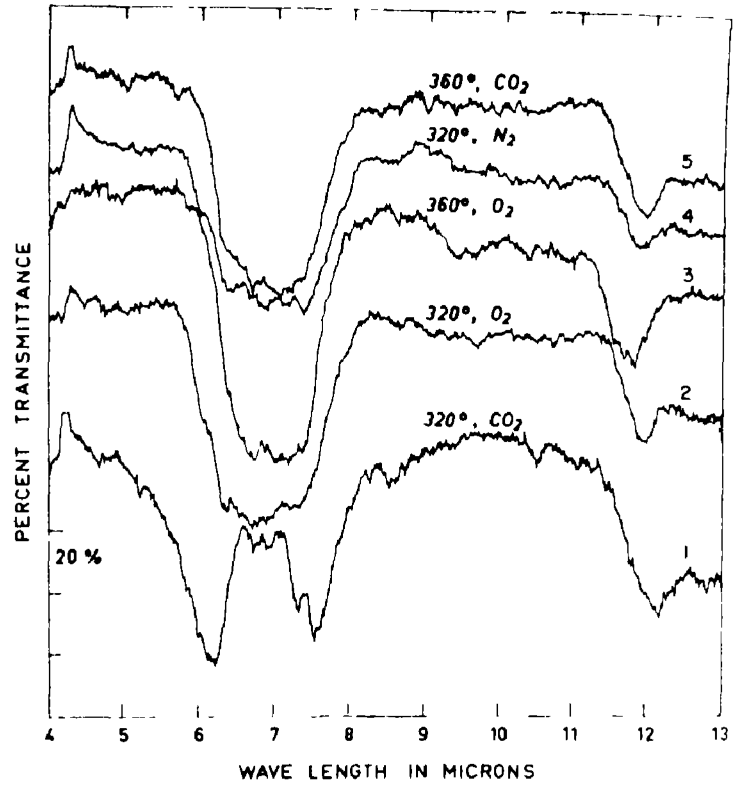


FIG 1 Infra-red spectra of residues obtained on heating $Eu_2Ox_3\ 5\ 8H_2O$ at the temperatures and in the atmospheres indicated on each curve (For suggested composition see Table 1)

either $Eu_2(CO_3)_3$ or EuOx, but the very low per cent of CO_2 in the non-reductive residue (1 9 per cent) indicates the choice of the latter, reaction (1) being followed by air oxidation and an initial decomposition to the carbonate

$$4EuOx + O_2 \rightarrow 2(EuOx)_2O \qquad (2)$$

and

$$(EuOx)_2O \rightarrow (EuCO_3)_2O + 2CO \qquad (3)$$

At 320° reaction (3) was almost completed and the residue contained 18 8% CO (theoretical 20%) Fig 1, curve 2 shows the infra-red absorption of the carbonat (with only remnants of the oxalate) in the residue obtained from the parallel experiment at 320° in an atmosphere of oxygen

At 360° in an atmosphere of air or oxygen, another intermediary oxycarbonat $(EuO)_2CO_3$, was obtained (see Fig 1, curve 3), and at 390° the white oxide Eu_2O_3 w formed

In an atmosphere of nitrogen the oxidation step (2) was missing, and the sequen of decomposition reactions seemed to proceed at a somewhat slower rate EuC (see Fig 1, curve 4), $Eu_2O\ CO_3$ and EuO were the main products at 320°, 360° and 3 respectively

Carbon dioxide retarded the decomposition of the oxalate as well as that of t carbonate The composition of the residues of ignitions in carbon dioxide we EuOx, $EuCO_3$ (see Fig 1, curve 5), $Eu_2\ O\ CO_3$ and EuO (?) at 320°, 360°, 390° a

420° respectively The colouration of the residues indicates that the thermal decomposition of europium oxalate to the carbonate is attended with disproportionation of the evolving carbon monoxide, as in the case of all other oxalates

Lastly, the appearance of a transmission peak at 4.2-4.3 μ in the infra-red spectra of all decomposition residues which were known to contain the europous ion is remarkable

(b) *Decomposition curves in vacuum*

The curves in vacuum are shown in Fig 2 For the sake of comparison, the pressures were plotted as calculated for standard samples weighing 6 mg each The partial pressures of CO and CO_2 evolved on heating at the temperatures and for the times indicated are recorded in Table 3 These values are given in percentages of the expected pressures if each mole of europium(III) oxalate were to yield 3 moles of CO and 3 moles of CO_2 on decomposition The total volume of the vacuum apparatus was 4754 ml, hence a 10 mg sample should give partial pressures equal to 203 mμ at room temperature (20 C)

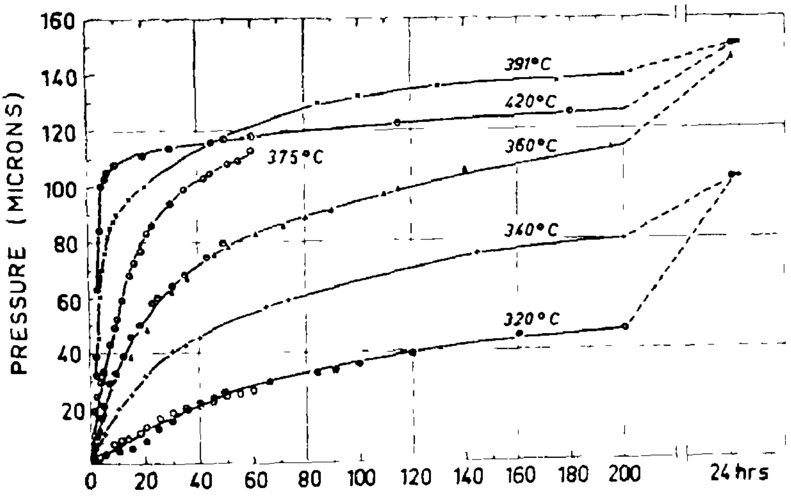


FIG 2 - Decomposition curves of Eu_2Ox_3 in vacuum (pressures were standardized for 6 mg samples)

The ratio of CO_2/CO ($= R'$) evolved in short times as may be seen in Table 3 is more than three, decreasing after 24 hr to nearly two This is in accord with the reducing power of the residues and with the assumption that (1) is the first and main reaction

$$Eu_2Ox_3 \rightarrow 2EuOx + 2CO_2 \qquad (1)$$

The origin of CO is reaction (4), proceeding simultaneously with (1) at a slower rate, and being completed much later

$$EuOx \rightarrow EuCO_3 + CO \qquad (4)$$

Any other sequence of reactions in which decomposition to an oxycarbonate or the oxide is the last step would with time have caused an increase in the proportion of CO_2

It also appears on comparing the ratios R′ for short times at increasing temperatures that the temperature coefficient for reaction (1) is somewhat greater than that for reaction (4) Values of R', as well as the decomposition rates, are poorly reproducible.

TABLE 3. PARTIAL PRESSURES OF CO AND CO_2 EVOLVED ON HEATING Eu_2Ox_3 IN VACUUM EXPRESSED IN MOLE PER CENT

°C	Sample wt. (mg)	Time of heating	CO_2 (%)	CO (%)	No. infra-red* spectrum
320	6.25	30 min	33.3	9.9	1
	7.12	60 min	40.4	13.6	
	6.32	23 hr	58.2	27.0	2
	6.18	24 hr	59.0	25.5	
360	5.08	30 min	51.1	16.5	
	6.27	60 min	51.5	15.9	
	6.96	24 hr	74.9	34.4	
	6.18	24 hr	82.3	36.7	5
375	5.73	30 min	55.1	16.4	
	5.32	60 min	69.7	21.6	3
391	5.25	60 min	74.7	20.8	4
	7.36	60 min	55.4	19.0	
	6.32	23 hr	86.1	38.4	
	6.13	24 hr	88.2	28.4	6
420	7.79	10 min	66.4	24.7	
	6.40	22 hr	82.1	39.9	7

* See Fig. 3.

the experimental inconsistency being probably connected with the timing of reaction (4), i.e. the stage of reaction (1) at which (4) sets in.

Further, one may conclude that reaction (4) is accompanied by disproportionation of CO: 2CO → CO_2 + C (5), whenever %CO_2 66.7 %CO. For example, in the case of the last experiment recorded in the table, at 420°, 66.7 − 39.9 = 26.8% CO underwent disproportionation. Adding half of this value to the 66.7% CO_2 from reaction (1), one obtains 80.1% CO_2, in fairly good agreement with the measured result. Disproportionation is also indicated by the brown colouration of the residues.

Thus in the temperature range 360–420°, Eu(II)CO_3 (admixed with some carbon) was formed after prolonged heating, but at 320° a tendency to the formation of the carbonato-oxalate Eu_2OxCO_3 may be assumed, neither of the two reactions having been completed after heating for 23 hr.

The infra-red spectra (see Fig. 3) of the residues conform qualitatively to the above conclusions. For purposes of identification, the numbering given in Fig. 3 appears in the last column of Table 3. On spectrum No. 1 (320°, 30 min) the presence of the small amount of carbonate is inappreciable, and only the absorption bands of the oxalate are visible. In spectra Nos. 2 and 3 (320° and 375°) the absorption band of the oxalate still preponderate, and No. 4 (391°) indicates a mixture of the two anions, in spite of the high percentage of CO_2 that has evolved. Spectra Nos. 5 and 6 (360° and 391°, 24 hr) show only traces of the oxalate ion, and No. 7 (420°) is that of pure carbonate.

The stability of $EuCO_3$ in vacuum compared to its instability in an atmosphere of CO_2 is remarkable. This anomaly was earlier observed in our study on the thermal decomposition of yttrium oxalate[12] and was attributed to the stabilization of the carbonate by the carbon deposited from disproportionation, probably forming a complex carbonaceous anion.

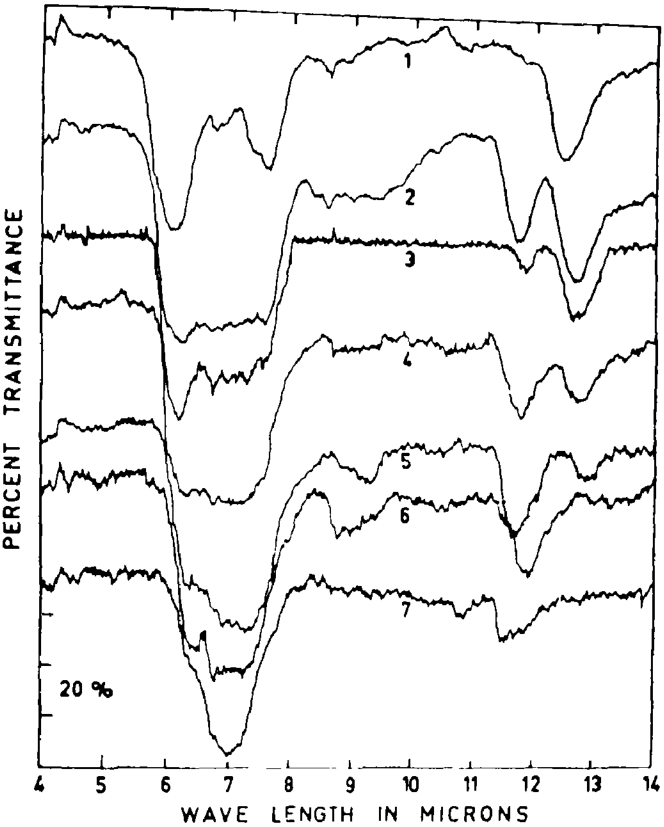


Fig. 3 Infra-red spectra of residues obtained on heating Eu_2Ox_3 in vacuum Temperatures and time of heating are shown in Table 3

On heating a residue of $Eu(II)CO_3$ (obtained in vacuum as above) at a temperature above 500°, the gas evolved is mostly CO and the ratio R' is reversed [13]

An example of decomposition of Eu_2Ox_3 at high temperatures is given in Table 4 A sample weighing 2.75 mg was heated intermittently for 24 hr at each temperature

Table 4 – Mole per cent of CO and CO_2 evolved on heating Eu_2Ox_3 in vacuum at high temperatures

°C	CO (μ)	CO_2 (μ)	CO (%)	% CO_2 (%)
500	24	53	43.0	95.0
850	30	5	53.8	9.0
Total	54	58	96.8	104.0

Evidently, both the europous ion as well as the deposited carbon are re-oxidized on decomposition of the divalent carbonate formed at the lower temperature A preparation of pure $Eu(II)CO_3$ (to be reported elsewhere), was found to evolve, besides CO_2 an appreciable amount of CO even at 400°

DISCUSSION

All the experimental evidence without exception shows that the first step in the decomposition of Eu_2Ox_3, in vacuum as well as in various atmospheres is accompanied

---

[12] A Glasner, E Levy and M Steinberg, *J Inorg Nucl Chem* **25**, 1119 (1963)

[13] I G Berg and K A Buzdov, *Russian J Inorganic Chem* 6, 1025 (1961)

by the reduction of the europium to the divalent state Decomposition sets in at a rather low temperature (even at 250° after prolonged heating) as compared to the other light rare earth oxalates, which will decompose⁽²⁾ only above 340° The evolving gases are composed mainly of CO_2, and less than 25% CO

Decomposition of Eu(II)Ox to the carbonate takes place at a very slow rate at temperatures above 320° The evolving CO disproportionates to the extent of $\sim\frac{2}{5}$ of the total CO This ratio is less than the disproportionation found to occur ($\sim\frac{3}{5}$) with Sm_2Ox_3 and Gd_2Ox_3 ⁽²⁾ Probably only that part of the CO disproportionates which is evolved after the abatement of reaction (1), but not the portion evolving simultaneously with reaction (1)

Europous carbonate (or oxalate) is oxidized in a stream of air (or oxygen) and soon decomposition to Eu_2O_3 follows In vacuum the carbonate is stabilized by the deposited carbon

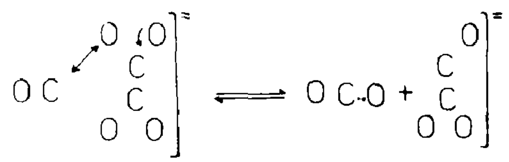
Evidently, whenever an oxalate decomposes, a portion of the CO is oxidized to CO_2, leaving a reduced solid residue, reduction of the cation occurs if it is reducible, otherwise a reduced anion is formed Hence, a unified reaction mechanism is suggested for all oxalate decompositions as follows

$$\text{a) } Ox^{2-} \rightarrow CO_3^{2-} + CO$$

$$\text{b1) } Ox^{2-} + CO \rightarrow C_2O_3^{2-} + CO_2$$

The latter reaction may be represented electronically

b1)

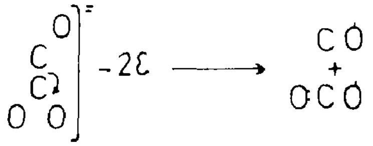


Both reactions may take place to some extent at low temperatures, but the gases are trapped in the solid and do not evolve unless a critical pressure is attained, at a sufficiently high temperature

If the metal is reducible, reaction b) will take a different course

$$\text{b2) } Ox^{2-} + CO - 2e \rightarrow 2CO_2 + CO$$

b2)



In this case, CO is reproduced in addition to two molecules of CO_2, hence th action of CO is catalytic, and the critical decomposition pressure is attained at lower temperature This catalytic effect explains the decomposition of Eu_2Ox_3 w below 300°, as well as the decomposition of other oxalates of reducible cations (such nickel⁽⁴⁾ and ferric⁽⁵⁾ oxalate) at comparable temperatures

The anion $C_2O_3^{2-}$ appears to be stable to heat up to ~700°, when it decompos evolving CO $C_2O_3^{2-} \rightarrow O^{2-} + 2CO$ (The possibility that reaction b1) repe itself, forming $C_2O_2^{2-}$, should also be considered) In air it may be oxidized w evolution of CO_2 at a lower temperature $C_2O_3^{2-}$ is also resistant to the action acids, but dissolves on heating,⁽¹,¹⁴⁾ releasing CO

⁽¹⁴⁾ P L GUNTHER and H REHAAG, *Ber Dtsch Chem Ges*, 71 B, 1771 (1938)

J Inorg Nucl Chem 1963 Vol 25, pp 1423 to 1429 Pergamon Press Ltd Printed in Northern Ireland

HEATS OF FORMATION OF $Pu_{(aq)}^{3+}$, $PuCl_{3(c)}$, $PuOCl_{(c)}$, $Am^{3+}_{(aq)}$, $AmCl_{3(c)}$ AND $AmOCl_{(c)}$ *

J Fuger† and B B Cunningham
Department of Chemistry and Lawrence Radiation Laboratory
University of California
Berkeley California

(*Received* 22 *March* 1963)

Abstract—The following heats of solution have been measured alpha plutonium in 6 M HCl, 138.90 ± 0.9, alpha plutonium in 1.5 M HCl, 138.65 ± 0.7, $PuCl_{3(c)}$ in 0.001 M $HClO_4$ 0.099 M NH_4ClO_4, −31.60 ± 0.35, $AmCl_{3(c)}$ in 1.5 M HCl, 30.60 ± 0.2, $AmCl_{3(c)}$ in 0.001 M HCl −33.36 ± 0.25 kcal mole^{-1} respectively

On combination with other thermodynamic data these results yield the following standard heats of formation at 298 K $Pu^{3+}_{(aq)}$ 138.6 ± 0.7 $PuCl_{3(c)}$ 226.8 ± 0.7, $PuOCl_{(c)}$ 219.7 ± 1, $Am^{3+}_{(aq)}$, −162.4 ± 3, $AmCl_{3(c)}$ 249.2 ± 3 $AmOCl_{(c)}$, 227.6 ± 3, all in kcal per mole

INTRODUCTION

Much of the available thermochemical data on the transuranium elements is based on measurements carried out a number of years ago when the samples of these materials were very small and often inadequately characterized as to crystallographic homogeneity or chemical purity Because of the now increased availability of some of these elements in highly purified form a remeasurement of values seems desirable For example, the only published value for the heat of solution of plutonium metal is that of Westrum and Robinson[1] who reported −141.64 ± 0.2 kcal mol^{-1} in 6 M HCl However, owing to the early date at which these measurements were carried out no statement could be made concerning the allotropic form of the metal used Since plutonium metal is now known to exist in six distinct crystallographic forms, some of which may be stabilized by relatively minor amounts of impurities and since the heats of transition from the alpha to epsilon phases sum to 1.7 kcal mol^{-1} the previously reported value could be in error by nearly 2 kcal

Again, the present values for the heats of formation of $Am^{3+}_{(aq)}$, $AmCl_{3(c)}$ and $AmOCl_{(c)}$ assume the heat of solution of $AmCl_{3(c)}$ to be the same as that of $PuCl_{3(c)}$ without experimental verification

The present paper reports a measurement of the heat of solution of highly purified alpha plutonium (kindly given to us by the Los Alamos Scientific Laboratory) in both 6 M and 1.5 M HCl as well as the heats of solution of $PuCl_{3(c)}$ in 0.099 M NH_4ClO_4-0.001 M $HClO_4$ and of $AmCl_{3(c)}$ in 1.5 M and 0.001 M HCl

---

* This work was done under the auspices of the United States Atomic Energy Commission

† Chercheur à l'Institut Interuniversitaire des Sciences Nucléaires Belgium which provided part of the financial support of this author Present Address Université de Liège Laboratoire Chimie Nucléaire, 2, Rue A Stevart Liège, Belgium

(1) E F Westrum, Jr and H P Robinson *Radiochemical Studies The Transuranium Elements* (Edited by G T Seaborg J J Katz and W M Manning) NNES Plutonium Project Record Div IV, Vol 14B, p 914 McGraw-Hill Book Company (1949)

EXPERIMENTAL

Materials

Plutonium metal. About 2 g of plutonium were furnished by Los Alamos with the identifying designation "A.E.C. 437-SAN-5000-11, HOO 572124-PMR-22". The sample was in the form of a single piece of metal and was labeled as the alpha (monoclinic) form. The X-ray diffraction pattern obtained by us from a small piece of the sample was consistent with the data[2] reported for the structure of alpha plutonium. As a further check on the structure a density determination was carried out on the main piece. The density was found to be 19.8 ± 0.2 g cm^{-3} in good agreement with the bulk density value of 19.63 g cm^{-3}, reported[3] for the alpha form.

The chemical purity of the metal, as determined at Los Alamos, is indicated by the data listed in Table 1.

TABLE 1 — ANALYSIS OF HIGH PURITY ALPHA PLUTONIUM
(results expressed in p.p.m.)

Li	0.2	Si	10	Bi	1	B	0.5	W	40
Be	0.1	Pb	2	Co	10	F	2	Zr	5
Na	10	Cu	2	Zn	10	Ni	20	Th	40
Ca	10	Cr	10	C	40	U	25	Mg	5
Al	25	Mn	1	O	90	Am	0.044	Pu	99.98%
La	10	Sn	1	Fe	45	Ta	35		

Note. The numbers following ' ' are limits of detection.

Because of the extreme hardness of alpha plutonium we found it necessary to fracture, rather than cut the large piece to obtain samples for calorimeter runs. This was done by wrapping the piece in tungsten foil and applying pressure. The smaller pieces were inspected microscopically for cleanliness before weighing on a quartz fibre torsion balance (Rodder Model I Microtech Services Company, Berkeley, California) sensitive to ~0.05 μg.

The samples were weighed in air and were then sealed into pyrex calorimeter bulbs in a dry argon atmosphere, by heating in the neck of the bulb a pyrex bead coated with Apiezon W wax.

Plutonium and americium trichlorides. The starting materials were HCl solutions of the chlorides purified by ion exchange. These solutions were evaporated to dryness *in a stream of* $HCl_{(g)}$, sublimed in vacuum and finally grown in the form of a single crystal by the technique of gradient solidification from the melt, as described by GRUEN *et al.*[4] for lanthanum trichloride. Under the conditions described the hexagonal trichlorides yield a single oriented crystal, the *c*-axis being parallel to the temperature gradient of the furnace. About 100 μg pieces of these crystals were analysed by copper spark spectrographic emission analysis. No impurities were detected* in these samples.

The plutonium trichloride used for the calorimeter measurements was taken from a single crystal grown as described and weighing about 2.5 g. The AmCl$_3$ single crystal weighed about 0.7 g.

* Limits of detection (in μg) by this method are as follows:

0.01—Ag, Al, Ba, Be, Ca, Cr, Eu, Fe, Ga, La, Mg, Mn, Mo, Nb, Sc, Si, Sr, Ti, Yb, Y, Zr

0.05—Am, Bi, Co, Dy, Er, Gd, Ge, Hf, Ho, In, Lu, Ni, Sm, Tm,

0.1—Ce, Nd, Np, Os, Pb, Pd, Pr, Pt, Re, Rh, Ru, Sn, Ta, Tl, W, Zn,

0.5—As, Ir, Pu, Sb, Tb, Th, U,

1—Au, Cm, K, Na

Barium was determined specially in its most sensitive wavelength region. Hg, Li, P, Te, Co, Rb were not analysed for, nor was copper, obviously. Pulse analysis showed the samples to be free of significant amounts of extraneous α-emitters.

[2] (a) W. H. ZACHARIASEN in "*The Metal Plutonium*" (Edited by A. S. COFFINBERRY and W. MINER) Chapt. 10, University of Chicago Press (1961).
(b) F. ANSELIN, *Ibid.* Chapt. 11.

[3] J. A. LEE and P. G. MARDON, in *The Metal Plutonium* (Edited by A. S. COFFINBERRY and W. MINER) Chapt. 14, University of Chicago Press (1961).

[4] D. M. GRUEN, J. G. CONWAY, R. D. MCLAUGHLIN and B. B. CUNNINGHAM, *J. Chem. Phys.* 1115 (1956).

Due to the marked hygroscopicity of the trichlorides, special care was taken to handle them in a suitably dry nitrogen atmosphere, produced by boiling the liquid and subsequently passing the gas through a trap at near liquid nitrogen temperature. The dry nitrogen was introduced at a high flow rate into a metallic gloved box in which the samples were prepared. Items were introduced by means of a vacuum lock. The samples (one or two pieces) were sealed into Pyrex calorimeter bulbs of known volume using a Pyrex bead coated with Apiezon W and a hot wire.

The weighings were made to a few micrograms accuracy on an Ainsworth Type V. M. Assay balance. Each gross and tare weighing was repeated at least four times. Corrections were made for differences in density between air and nitrogen and the weight finally reduced to weight in vacuum.

Solutions. Solutions of HCl, $HClO_4$ and $HClO_4$–NH_4ClO_4 were prepared from analytical grade reagents. The acids were standardized volumetrically to within ±0.2 per cent against constant boiling sulphuric acid. Solvent acids for $PuCl_{3(c)}$ and $AmCl_{3(c)}$ were previously de-aerated with argon. Plutonium metal was dissolved in air-free acid saturated with hydrogen. The solutions were loaded and the calorimeter assembled in a gloved box which had been flushed with argon for several hours. Mass analysis of the atmosphere of the box at time of loading indicated that the oxygen content was less than 0.02 volume per cent. Although no oxidation to Pu^{4+} was to be expected under the conditions of our experiments the solutions were checked spectrophotometrically, with a Cary Model 14 Recording Spectrophotometer. Only trivalent plutonium was found in the calorimeter solutions (limit of detection of Pu^{4+} approximately 1 per cent). We also checked the completeness of dissolution of plutonium metal in 1.5 M HCl by centrifuging the calorimeter solution and checking for α-activity in the microscopic amount of washed solid residue. No plutonium-containing solid was detected.

Calorimeter

Some features of the microcalorimeter used for our measurements have been described previously[6] but the instrument has since been modified to increase its stability and to convert it to a recording instrument. These modifications will be described in detail elsewhere.[7] It will suffice here to state that it has a heat capacity of approximately 9 cal, a temperature sensitivity of approximately 1×10^{-5} °C and a thermal leakage modulus of about 5×10^{-4} min^{-1}. It was thermostated at 25.03°C, but the steady state temperature was from 0.1 to 0.3° higher due to radioactive heating, power input to bridge, etc. In some of our measurements the heat of breakage of the calorimeter bulbs was an important limitation on the accuracy of the measurements. Typically this heat effect, determined by breaking several bulbs containing a small amount of water, was found to amount to $(6 \pm 3) \times 10^{-4}$ cal $bulb^{-1}$. This correction was applied to all measurements. In addition the results were corrected where necessary, for the heat of saturation by $H_2O_{(g)}$ and $HCl_{(g)}$ of the dry gas enclosed initially in the calorimeter bulbs, and for the saturation of the hydrogen evolved from the metal. In all measurements the heat evolution was complete within 3 min.

A potential divider in the calorimeter circuit allowed a continuous recording of the calorimeter chamber temperature, hence the computation of accurate corrections for thermal leakage. Heat inputs of the order of 0.2 calorie were reproducible to ±0.1 per cent. Usually three or more heat inputs preceded a chemical reaction and three followed it.

As a final check on the performance of the calorimeter a number of runs were made on the heat of solution of pure Mg metal in 1 M HCl. The results are given in Table 2. The average of these values is in reasonable agreement with the figure of −111.322 ± 0.041 kcal determined on a much bigger scale by SHOMATE and HUFFMAN.[8]

Units, auxiliary thermodynamic and limits of error

In our thermochemical calculations we have taken the calorie to be equal to 4.1840 absolute joules.

The limits of error quoted for our experimental data are for the 95 per cent confidence interval.

---

[5] E. F. WESTRUM, JR. and L. EYRING, *J. Amer. Chem. Soc.* **74**, 2045 (1952).

[6] (a) S. R. GUNN, Report UCRL-2541 (1954).
(b) S. R. GUNN and B. B. CUNNINGHAM, *J. Amer. Chem. Soc.* **79**, 1563 (1957).

[7] J. FUGER, J. L. BURNETT and B. B. CUNNINGHAM, Report UCRL (to be published).

[8] C. H. SHOMATE and E. F. HUFFMAN, *J. Amer. Chem. Soc.* **65**, 1625 (1943).

TABLE 2 — HEAT OF SOLUTION OF MAGNESIUM METAL IN 1 M HCl

	Weight of sample (μg)	Heat evolved (Cal)	$\Delta H_{298\ 3}$ (kcal mole $^{-1}$)
1	51 97	0 2377	−111 20
2	65 85	0 3023	- 111 61
3	84 17	0 3846	-111 10
		Average	111 30 ± 0 56

TABLE 3 - HEAT OF SOLUTION OF ALPHA PLUTONIUM METAL IN HCl SOLUTION

Medium	Weight of sample (μg)	Pu^{3+} (M)	Heat evolved (Cal)	$\Delta H_{298\ 3}$ (kcal mole $^{-1}$)
HCl 1 500 M	494 7	2 587 10^{1}	0 2877	139 0
HCl 1 500 M	597 5	3 124 10^{1}	0 3454	138 2
HCl 1 500 M	590 3	3 087 10^{1}	0 3413	138 2
HCl 1 500 M	901 2	4 712 10^{1}	0 5247	139 2
			Average	138 65 0 7
HCl 6 00 M	696 8	3 643 10^{1}	0 4042	138 7
HCl 6 00 M	586 6	3 067 10^{1}	0 3413	139 1
			Average	138 90 ± 0 9

but we have not attempted to retain this limit when combining our data with that from other sources for which we take the error to be that stated by the author

The heat measurements reported here were made at temperatures a few tenths of a degree above 298 16 K but within their limits of error they are not distinguishable from 298 16 K values Hence, we have treated them as such

On the basis of mass analysis data we calculate 239 11 and 241 07 respectively for the atomic weights of the plutonium and americium stocks used

All auxiliary thermodynamic data for which no reference is given have been taken from *Selected Values of Chemical Thermodynamic Properties*, U S Bureau of Standards Circular 500 (1952)

RESULTS AND DISCUSSION

The experimentally observed heats of solution of alpha plutonium are tabulated in Table 3

Our value of -138 90 ± 0 9 kcal mol^{-1} for the heat of solution of alpha plutonium metal in 6 M HCl may be compared directly with that of 141 64 ± 0 2 reported WESTRUM and ROBINSON$^{(1)}$ A part of the discrepancy of 2 74 kcal mole^{-1} may be explained by the fact that early microscale preparations of plutonium yielded malleable metal of density ca 16, which corresponds to one of the phases δ, δ' ϵ—all of which have a substantially higher heat content than that of the alpha pha

If we assume WESTRUM and ROBINSON'S metal to have been pure epsilon, the h of transformation reported by KAY$^{(9)}$ give a calculated heat content of 1 74 kcal mol above that of the alpha phase We are unable to account for the remaining kilocalorie difference It is of course remarkable that WESTRUM and ROBINSON

---

(9) A E KAY, *The Metal Plutonium* (Edited by A S COFFINBERRY and W M MINER) Chap The University of Chicago Press (1961)

able to obtain such reliable results at a time when almost nothing was known about the properties of plutonium metal

Our experimental heat in 6 M HCl corresponds to the reaction

$$Pu_{(c\ \alpha)} + \sim 20000[HCl\ 8\ 105H_2O] \rightarrow$$
$$[PuCl_3 \text{ in } \sim(20000-3)HCl\ 162000\ H_2O] + \tfrac{3}{2}H_{2(g)}$$

Neglecting the slight change in composition of the 6 M HCl due to consumption of HCl in the dissolution of the metal and taking the relative heat content of HCl in 6 M HCl ($HCl\ 8\ 105\ H_2O$) to be $-36\ 81$ kcal mole^{-1}, we calculate the heat of formation of $PuCl_3$ in $\sim 20000[HCl\ 8\ 105\ H_2O]$ to be 249 33 0 9 kcal mole^{-1} The calculation also ignores the influence of very low concentrations of $PuCl_3$ on the HCl heat content

TABLE 4 — HEAT OF SOLUTION OF $PuCl_{3(c)}$ IN 0 001 M HCl, 0 099 NH_4ClO_4

Weight of sample (mg)	Pu^{3+} (M)	Heat evolved (Cal)	ΔH_{soln} (kcal mol^{-1})
3 976 0 005	1 439 10 $^{-3}$ M	0 3637	31 61
4 733 0 005	1 713 10 $^{-3}$ M	0 4310	31 46
5 727 0 005	2 072 10 $^{-3}$ M	0 5271	31 80
		Weighted average	31 60 0 35

WESTRUM and ROBINSON[(10)] measured the heat of solution of $PuCl_{3(c)}$ in various concentrations of HCl They report values of 22 15 0 1 kcal mole^{-1} in 6 M HCl, 29 5 ± 0 1 in 1 5 M HCl and 31 76 0 1 in 0 1 M HCl

We have measured the heat of solution of $PuCl_{3(c)}$ in 0 001 M $HClO_4$–0 099 M NH_4ClO_4 with the results shown in Table 4

Our value for the heat of solution of $PuCl_{3(c)}$ in very dilute acid agrees with that of WESTRUM and ROBINSON in 0 1 M HCl well within the accuracy of the measurements We therefore believe their results at other HCl concentrations to be accurate

For the process

$$PuCl_{3(c)} + xHCl\ 8\ 105\ H_2O \quad PuCl_3 \text{ in } xHCl\ 8\ 105\ H_2O$$

WESTRUM and ROBINSON report 22 15 0 1 kcal mole^{-1} From this and our metal data in 6 M HCl we calculate the heat of formation of $PuCl_{3(c)}$ to be 227 2 0 9 kcal mole^{-1}

From our measurements on the heat of solution of the metal in 1 5 M HCl and WESTRUM and ROBINSON's value for the heat of solution of $PuCl_{3(c)}$ in 1 5 M HCl we calculate $\Delta H^{\circ}_{f\,PuCl_{3(c)}}$ $-$ 226 6 0 7 kcal mole^{-1} Weighting each of the two values in proportion to the numbers of observations on which it is based gives 226 8 ± 0 7 kcal mole^{-1} as our best value for the heat of formation of $PuCl_{3(c)}$ This value

---

[(10)] E F WESTRUM, JR and H P ROBINSON *Radiochemical Studies The Transuranium Elements* (Edited by G T SEABORG J J KATZ and W M MANNING) Plutonium Project Record NNES, DIV IV, Vol 14-B, p 922 McGraw-Hill New York (1949) may be combined with the value of 20.8 ± 0.7 kcal for the heat of the reaction

$$PuCl_{3(c)} + H_2O_{(g)} = PuOCl_{(c)} + 2HCl_{(g)}$$

reported by SHIFT and DAVIDSON(11) to give a corrected value, −219.7 ± 1 kcal mole^{-1}, for the heat of formation of $PuOCl_{(c)}$

Extrapolation of the heat of solution data for $PuCl_{3(c)}$ obtained by WESTRUM and ROBINSON gives for the heat of solution of $PuCl_{3(c)}$ at infinite dilution −31.9 ± 0.2 kcal mole^{-1} Combining our value for the heat of formation of $PuCl_{3(c)}$ with this datum gives for $Pu^{3+}_{(aq)}$, $\Delta H^{\circ}_{f_{Pu^{3+}(aq)}} = -138.6 \pm 0.7$ kcal mole^{-1}

LOHR and CUNNINGHAM(12) measured the heat of solution of americium metal, of unspecified crystal structure, in 1.5 M HCl and reported −162.3 ± 2.7 kcal mole^{-1} for the solution reaction

TABLE 5.—HEAT OF SOLUTION OF $AmCl_{3(c)}$ IN HCl SOLUTIONS

Medium	Weight of sample (mg)	Am^{3+} M	Heat evolved (Cal)	$\Delta H_{298.1}$ (kcal mole^{-1})
HCl 10^{-3} M	6.138 ± 0.004	2.207×10^{-3}	0.5900	33.40
HCl 10^{-3} M	6.677 ± 0.005	2.402×10^{-3}	0.6402	33.31
			Average	33.36 ± 0.25
HCl 1.500 M	7.193 ± 0.006	2.588×10^{-3}	0.6317	−30.51
HCl 1.500 M	7.336 ± 0.007	2.639×10^{-3}	0.6478	30.68
HCl 1.500 M	5.683 ± 0.004	2.045×10^{-3}	0.5007	30.61
			Average	30.60 ± 0.20

It is now known(13) that the room temperature stable modification of americium is a double hexagonal close packed phase and that this is normally obtained in small scale reductions It is likely that this was the form of americium metal used in the heat-of-solution measurements It is our intention to repeat the measurements using americium metal of known crystallographic form, but for the present we wish only to report our values for the heat of solution of $AmCl_{3(c)}$ in HCl solutions As mentioned previously, the samples used for the heat measurements were chipped from a single 0.7 g crystal of $AmCl_3$ having the hexagonal $LaCl_3$ type of structure

The thermochemical data are summarized in Table 5 In calculating their values for the heats of formation of $AmCl_{3(c)}$ and $Am^{3+}_{(aq)}$, LOHR and CUNNINGHAM took the heats-of-solution of $AmCl_{3(c)}$ in HCl solutions of various concentrations to be the same as those for plutonium trichloride As is evident from Table 5 they are actually about 1.1 kcal more negative From a compilation of data assembled by SPEDDING and FLYNN(14), the heats of solution of the light rare earth trichlorides (which are isostructural with $PuCl_3$ and $AmCl_3$) are shown to become increasingly negative by about 1.3 kcal per unit increase in atomic number

(11) J SHIFT and N R DAVIDSON, *Radiochemical Studies The Transuranium Elements* (Editors G T SEABORG, J J KATZ and W M MANNING) NNES, Plutonium Project Record, Div Vol 14B, p 841 McGraw-Hill, New York (1949)

(12) H R LOHR and B B CUNNINGHAM, *J Amer Chem Soc* 73, 2025 (1951)

(13) D B MCWHAN, J C WALLMANN, B B CUNNINGHAM, L B ASPREY, F H ELLINGER W H ZACHARIASEN, *J Inorg Nucl Chem* 15, 185 (1960)

(14) F H SPEDDING and J P FLYNN *J Amer Chem Soc* 76, 1477 (1953)

Using our value for the heat of solution of $AmCl_{3(c)}$ in 1.5 M HCl and the value of −162.3 for the heat of solution of americium metal in 1.5 M HCl, we calculate

$$\Delta H^{\circ}_{f_{AmCl_{3(c)}}} = -249.2 \pm 3 \text{ kcal mole}^{-1}$$

Taking −33.36 ± 0.25 for the heat of solution of $AmCl_{3(c)}$ in 10^{-3} M HCl to be equivalent to that at infinite dilution, we find

$$\Delta H^{\circ}_{f_{Am^{3+}_{(aq)}}} = -162.4 \pm 3 \text{ kcal mole}^{-1}$$

Finally, using the data reported by KOCH and CUNNINGHAM[(15)] on the temperature dependence of the equilibrium constant for the reaction,

$$AmCl_{3(c)} + H_2O_{(g)} = AmOCl_{(c)} + 2HCl_{(g)}$$

we obtain

$$\Delta H^{\circ}_{f_{AmOCl_{(c)}}} = -227.6 \pm 3 \text{ kcal mole}^{-1}$$

Acknowledgements We wish to thank Mr. G. V. SHALIMOFF for performing numerous spectrographic analyses for us and Mrs. G. BOLZ of the Health Chemistry Group for providing assistance in handling radioactive materials

We are especially grateful to Mr. H. P. ROBINSON for assistance in maintenance of the calorimeter

---

(15) C. W. KOCH and B. B. CUNNINGHAM *J. Amer. Chem. Soc.* **76**, 1470 (1954)

J Inorg Nucl Chem 1963, Vol 25 pp 1431 to 1444 Pergamon Press Ltd Printed in Northern Ireland

RATES OF ISOTOPIC LIGAND EXCHANGE OF Ni(II) COMPLEXES OF γ-AMINEOXIMES(1)

D L Lewis and R K Murmann
Department of Chemistry, University of Missouri Columbia Missouri

(*Received* 21 *December* 1962, *in revised form* 8 *April* 1963)

Abstract The kinetics of the ligand exchange of $[\mathrm{Ni(AO)_2{-}H}]^+$ $[\mathrm{Ni(MeAO)_2{-}H}]^+$ and $[\mathrm{Ni(EnAO)-H}]^+$ have been investigated using C^{14} labeled ligands It was found that the exchange for the series follows the general law $R = k_1[\text{complex}]_T + k_2[\text{complex}]_T[\text{ligand}]_F$ The overall rates are in the order AO > MeAO > EnAO With $[\mathrm{Ni(AO)_2{-}H}]^+$ the exchange is rapid and carried predominately by the ligand dependent, k_2 term With $[\mathrm{Ni(MeAO)_2{-}H}]^+$ at constant $[\mathrm{MeAO}]_T$, R shows a minimum in the region of pH 8 In the basic region the faster rate is due to increased free ligand concentration while the acidic catalysis is interpreted on the basis of a half-bonded intermediate For $[\mathrm{Ni(EnAO)-H}]^+$ the exchange is carried by the k_1 term with k_2 being small The order of the ligand dependent step, k_2 is AO > MeAO > EnAO and is due to steric hindrance in the formation of a five co-ordinate activated state This is supported by the catalysis of exchange by foreign chelating ions or molecules These results are compared with the kinetics of reaction with EDTA and a mechanistic picture involving simple dissociation and a C N = 5 activated state is postulated and discussed

Isotopic ligand exchange studies have shown extreme utility in the clarification of mechanisms of reactions of coordination compounds There has been renewed interest in the planar state as a result of recent investigations on Ni(II), Pt(II) and Au(III) compounds (2 3 4) Of this group Ni(II) presents the most favourable characteristics for ligand exchange studies because of the relative speed of the reactions and the ease of following them Of the ligands which have been studied with Ni(II), CN (5) and ethylenediamine(5c 6) complexes show very fast exchange rates and are not suited for rigorous interpretation C-alkyl substitutions on ethylenediamine give complexes which show diminished rates (7) The insolubility of the dioxime complexes has prevented studies with these planar complexes in water solution

---

(1) Taken in part from the M A dissertation of D L Lewis Supported by the Division of Research Grants National Institute of Health (No A-3006) and by the University of Missouri Research Council Presented at the 14th Kansas City Amer Chem Soc Chemistry Conference November, 1962

(2) (a) F Basolo, H B Gray and R G Pearson *J Amer Chem Soc* **82**, 4200, (1960) (b) F Basolo, J Chatt H B Gray, R B Pearson and B L Shaw *J Chem Soc* 2207 (1961) (c) J Chatt and B L Shaw, *Ibid* 1718 (1960)

(3) (a) H B Gray, *J Amer Chem Soc* **84**, 1548 (1962) (b) H B Gray and R J Olcott, *Inorganic Chem* **1**, 481 (1962)

(4) R L Rich and H Taube, *J Phys Chem* **58**, 1 (1954)

(5) (a) A W Adamson, J P Welker and M Volpe *J Amer Chem Soc* **72**, 4030 (1950) (b) A G MacDiarmid and N F Hall, *Ibid* **76**, 4222 (1954) (c) F A Long, *Ibid* **73**, 537 (1951)

(6) D S Popplewell and R B Wilkins *J Amer Chem Soc* 4098 (1955) Although ethylenediamine-Ni(II) complexes are spin-free in solution, $[\mathrm{Ni(en)_2}]^{+2}(\mathrm{ClO_4})_2$ in the solid state is spin-paired H Glaser and P Pfeiffer *J Pract Chem* **153**, 300 (1939)

(7) (a) R G Wilkins, *J Chem Soc* 4521 (1957) (b) F Basolo, Y T Chen and R K Murmann *J Amer Chem Soc* **76**, 956 (1954)

Using aliphatic α-amineoximes, a series of Ni(II), spin-paired complexes have been prepared[8] which contain a hydrogen bond and thus are expected to be slower reacting than those of α-diamines. These compounds (Fig. 1) have a +1 charge and have suitable solubilities for precise studies. It was felt that a comparison of the

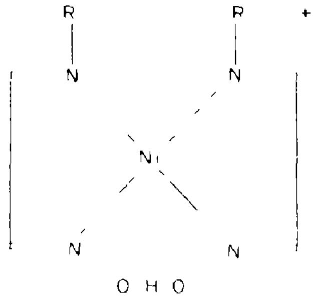


FIG. 1.—R = H, [Ni(AO)$_2$—H]; R = CH$_3$, [Ni(MeAO)$_2$—H];
R—R = —CH$_2$—CH$_2$—, [Ni(EnAO)—H].

previously published kinetics of acid dissociation[9] and EDTA reaction[9b] with those of ligand and metal ion isotopic exchange would provide considerable information about the mechanism of reaction used by planar Ni(II) compounds which, in a slightly modified way, may also be used by other planar d^8 ions. Also of interest is the magnitude of the modification of the exchange kinetics by the chelate ring formed with the hydrogen bond.

This paper reports isotopic ligand exchange studies and some ^{63}Ni exchange rates on [Ni(AO)$_2$—H]$^+$, [Ni(MeAO)$_2$—H] and [Ni(EnAO)—H].*

EXPERIMENTAL

AO and EnAO as well as their complexes [Ni(AO)$_2$—H]ClO$_4$ and [Ni(EnAO)—H]ClO$_4$ were prepared following methods previously described.[8] They were recrystallized from water until their visible and infrared spectra agreed with earlier analysed samples. MeAO was prepared by using methylamine in place of ammonia in the AO preparation. The free amineoxime was recrystallized from a benzene—petroleum ether "F" mixture giving colourless crystals, m.p. 68–69°C (Found: C, 54.08; H, 10.73; N, 20.67; Neut. Equiv., 130.5. Calc. for $C_6H_{14}N_2O$: C, 55.53; H, 10.84; N, 21.52; Neut. Equiv., 130.2).

[Ni(MeAO)$_2$—H]ClO$_4$ was prepared by a method similar to that used for the AO complex but a more careful neutralization to a pH of 7.5–8.0 was necessary. It was recrystallized from water giving yellow crystals soluble in acetone, alcohol and water having ϵ_{max} at 425 mμ = 121. Found: C, 35.12; H, 6.87; N, 13.45; Ni, 14.12; ClO$_4$, 24.24. Calc. for $C_{12}H_{27}N_4O_8NiCl$: C, 34.52; H, 6.52; N, 13.42; Ni, 14.06; ClO$_4$, 23.82%.) In the solid state the complex was found to be diamagnetic, χ_M = 192 × 10^{-6}, showing it to be in the spin-paired state as was observed with [Ni(AO)$_2$—H]$^+$ and [Ni(EnAO)—H].

Radioactive complexes

AO†, (NH$_2$—C(^{14}CH$_3$)$_2$—C(CH$_3$)=NOH, was prepared by the following procedure; the action of 1,3-^{14}C acetone on ethyl magnesium bromide in anhydrous ether, followed by hydrolysis gave

---

* In these formulas AO = 2-methyl-2-amino-3-butanone oxime, MeAO = 2-N-methylamino-2-methyl-3-butanone oxime, EnAO = 2,2'-ethylamino-bis-(2-methyl-3-butonone)-dioxime. The designation —H expresses the essentially complete ionization of a H$^+$ from the ligand in the formation of a hydrogen bond.

† An asterisk is used to denote that species containing ^{14}C.

(8) R. K. MURMANN, *J. Amer. Chem. Soc.* **79**, 521 (1957); **80**, 4174 (1958).

(9) (a) R. K. MURMANN, *J. Amer. Chem. Soc.* **84**, 1349 (1962); (b) *Inorg. Chem.* **2**, 116 (1963).

$CH_3CH_2-C(^{14}CH_3)(OH)$. This was dehydrated with 70% H_2SO_4 using a trace of I_2 as a catalyst giving primarily, $C(^{14}CH_3)_2=CH(CH_3)$ which was added to a slight excess of NOCl producing $C(^{14}CH_3)_2Cl-CH(CH_3)(NO)$. An excess of dry NH_3 in absolute CH_3OH was added to the nitrosyl chloride adduct and, after refluxing for several hours, the product $NH_2-C(^{14}CH_3)_2-C(CH_3)(=NOH)$ was reacted with a slight excess of Ni^{2+} at pH 7.5 and $[Ni(AO)_2-H]ClO_4$ was precipitated with an excess of $NaClO_4$. It was twice recrystallized from water, dried under vacuum and had an infra-red spectra identical with an authentic sample.

MeAO*, ($^{14}CH_3-NH-C(CH_3)_2-C(CH_3)=NOH$) was prepared from $^{14}CH_3NO_2$. Nitromethane-^{14}C was reduced with $SnCl_2$ in HCl to give methylamine-^{14}C which was steam distilled from basic solution into dilute HCl. $^{14}CH_3NH_3Cl$ was collected as a solid upon evaporation. This was equilibrated with normal CH_3NH_2 and the $^{14}CH_3NH_2$ formed added to anhydrous MeOH containing a slight excess of $C(CH_3)_2Cl-C(CH_3)(=NOH)$. After reaction, the solid product obtained upon evaporation was converted to $[Ni(MeAO)_2-H]ClO_4$ by stoichiometric amounts of $[Ni(H_2O)_6]Cl_2$ and NaOH solution followed by precipitation with an excess of $NaClO_4$. The complex, when recrystallized from water and dried, gave the same infrared spectra as an analysed non-radioactive sample.

A sample of $[Ni(MeAO)_2-H]ClO_4$ with a high specific activity was prepared by lowering the amount of inactive carbon introduced but, although it was reprecipitated several times, it still contained an impurity which catalysed the ligand exchange.

EnAO*, ($HON=C(CH_3)-C(CH_3)_2-NH-^{14}CH_2-^{14}CH_2-NH-C(CH_3)_2-C(CH_3)=NOH$) was prepared from 1,2-dibromoethane-1,2-^{14}C. Dibromoethane-^{14}C was treated in a bomb with anhydrous liquid NH_3 producing $NH_3Br-^{14}CH_2-^{14}CH_2-NH_3Br$. Addition of BaO produced anhydrous $H_2N-^{14}CH_2-^{14}CH_2-NH_2$ which was distilled into an anhydrous MeOH solution containing the calculated amount of $C(Cl)(CH_3)_2-C(CH_3)(=NOH)$. After heating and evaporation $[Ni(EnAO)-H]ClO_4$ was precipitated by the addition of Ni^{2+}, OH^- and excess $NaClO_4$. It was recrystallized from water and, after drying, gave a visible absorption spectra and molar absorbance identical to that of a sample of known purity.

All operations in the preparation of ^{14}C-ligands involving radioactive gases or volatile liquids were carried out in a high vacuum apparatus.

Visible absorption spectra were obtained with a Beckman Model DU Spectrophotometer equipped with "cell spacers" through which water at constant temperature could be pumped. Infra-red spectra in KBr pellets or Nujol mulls were obtained with a Perkin Elmer Infracord Model 137.

Carbon, hydrogen and nitrogen analyses were performed by Galbraith Laboratories, Knoxville, Tennessee, while nickel and ClO_4^- were determined gravimetrically using dimethylglyoxime and tetraphenyl arsonium chloride respectively.

A nuclear Chicago Model 151A scaler in conjunction with an ultra-thin mica window (1.1 mg/cm²) RCL Geiger Muller tube was employed for radio-assay of carbon-14 containing samples. Approximately 2 in. of lead shielding held the background to 20 ± 1 counts/min.

Exchange rate

The rate of ligand exchange was carried out by adding active complex to a solution containing inactive ligand and following the decrease in activity of the complex. Temperature of the exchanging solutions was controlled by thermostated baths with variations in the range of 2–30° of ±0.01° and ±1° in the 45–55° range. The half-time was obtained from a graph of log $(1-F)$ vs. time where F represents the fraction of exchange. The overall rate of exchange of labeled and unlabeled species was calculated from the McKAY equation[10] where† $a = 2[\text{AO complex}]_T + 2[\text{MeAO complex}]_T + [\text{EnAO complex}]_T$ and $b = [\text{ligand}]_T$.

$$R = \frac{\ln 2}{t_{1/2}} \frac{ab}{a+b}$$

Exchange was initiated by two methods: (a) a known amount of finely powdered complex was added to a solution containing a known amount of ligand at the desired pH. In most regions the ligand behaved as its own buffer. (b) A small amount of solution containing the high specific activity complex was injected into an equilibrated solution containing ligand and complex at known concentrations and pH. The complex added comprised only a small fraction of the total complex so that the equilibrium was not upset within the sensitivity of the measurements.

---

† The subscript T signifies the total concentration of all complex or ligand species.

[10] H. A. C. McKAY, *Nature, Lond.* **142**, 997 (1938).

In either case at appropriate times portions of the exchanging solution were withdrawn and the complex ion precipitated with a freshly prepared solution of Reinecke Salt, ($NH_4[Cr(NH_3)_2(SCN)_4]$). The precipitated complex was deposited on a thick, 1 in. circular, flat filter paper by the use of a glass chimney, washed with water, dried by suction and allowed to equilibrate with the atmosphere. The specific activity of the mats was measured using constant geometry and was corrected to infinite thickness using the weight of each mat and a calibration curve.

In several cases, the rate was simultaneously followed by measurements of the activity increase in the ligand. To do this the complex was removed in the usual way, the supernatant solution was made acidic, and a further quantity of Reinecke Salt added whereupon the protonated ligand Reineckate precipitated. It was converted into a mat and its specific activity at infinite thickness was measured. In all cases the rates obtained from the complex and from the ligand activity were identical.

Nickel exchange

^{63}Ni obtained from A.E.C., Oak Ridge, Tennessee contained some gamma emitters. It was purified by slow precipitation with dimethylglyoxime from a solution containing Fe^{3+}, Cr^{3+}, Mn^{2+} and Co^{2+}. A second precipitation followed by decomposition with concentrated $HClO_4$ gave a $Ni(ClO_4)_2$ solution of known concentration with only a small excess of $HClO_4$.

Metal ion exchange was initiated by the addition of a small amount of active nickel solution to a pre-equilibrated, thermostated, buffered (NH_4OAc) solution of the inactive complex and Ni(II). Portions of the complex were precipitated at measured intervals with Reinecke Salt and mounted as an infinitely thick mat. Measurements of the β- of ^{63}Ni were made with the same thin window Geiger tube as used for ^{14}C. In initial measurements, the rate was also followed by precipitating the Ni^{2+} with dimethylglyoxime, mounting and measuring its specific activity. The overall rate, R, was obtained from the slope of a graph of log(1 − *F*) versus Time using the familiar McKay equation.

RESULTS

$[Ni(AO^*)_2-H]^+ + 2AO \rightarrow [Ni(AO)_2-H]^+ + 2AO^*$. Graphs of log(1 − *F*) versus time were linear and extrapolated to a value of 1.0 for (1 − *F*) at time zero. Induced exchange due to precipitation and to the preparation of the complex for counting was zero within experimental error and the precipitating agent had no effect (runs 1, 3, 4). Table 1 contains the experiments which show that the rate constant,[14] using the expression, rate = $k[Ni(AO)_2-H]_T^+$ is strongly dependent on $[AO]_F$ and $[H^+]$ (runs 1, 2). However, the rate constant derived from the expression

$$R = k_2'[Ni(AO)_2-H^+]_T[AO]_F$$

is, within experimental error, a constant in the pH range (7.2–9.4) (runs 1, 2, 3, 4, 10, 15, 16). The half-times of exchange are small which made the experimental error somewhat larger than that observed with MeAO and EnAO so that the differences in k_2' are not significant. At 0° and μ approximately 0.03, k_2' has an average value of 1.4×10^3 l min^{-1} mole^{-1}. Since previous work had shown catalysis by small quantities of impurities, both $[Ni(AO)_2-H]^+$ and AO were recrystallized (runs 1–4). This did not affect k_2' indicating the absence of catalysts.

Runs 11–14 show the effect of foreign ions and molecules. Nitrate ion reduc the rate when in high concentrations (0.05 M) while NH_3–NH_4^+, 0.01 M, shows onl

---

[14] The designation used throughout this paper for rate constants will be for ligand exchange: the pseudo first order rate constant, *k*, defined as, overall rate, $R = k[\text{complex}]_T$, k_1 and k_2 defined by $R = k_1[\text{complex}]_T + k_2[\text{complex}]_T[\text{ligand}]_F$. For metal ion exchange, overall rate, $R = k'[\text{complex}]_T$. The term *free ligand* is meant to describe that which is uncomplexed and unpro nated. It is designated by the subscript *F*.

TABLE 1.—RATE OF LIGAND EXCHANGE OF $[Ni(AO)_2-H]$

$[Ni(AO)_2-H^+]_T = 5.14 \times 10^{-3}$ mole/l
$[AO]_T = 20.5 \times 10^{-3}$ mole/l

k defined as $R = k[Ni(AO)_2-H^+]_T$
k_2' defined as $R = k_2'[Ni(AO)_2-H^+]_T[AO]_{free}$

No.	T (°C)	pH	$[ligand]_{free}$ (× 10^3)		$t_{1/2}$ (min)	R (× 10^3) (mole l^{-1} min^{-1})	k (min^{-1})	k_2 (× 10^{-3}) l, min^{-1}, $mole^{-1}$
1*	0	9.15	3.60		0.15	32	6.2	1.7
2	0	9.41	1.44§		0.23	10.3	2.0	1.4
3*	0	9.15	3.60		0.14	34	6.6	1.8
4*§	0	7.06	3.56	× 10^{-2}	22	0.22	0.042	1.2
10	0	7.22	5.15	× 10^{-2}	11.1	0.43	0.084	1.62
15	0	7.86	2.04	× 10^{-1}	3.8	1.24	0.241	1.18
16	0	8.20	4.80	× 10^{-1}	1.33	3.56	0.619	1.29
5	2	7.06	3.56	× 10^{-2}	23	0.21	0.040	1.12
7	15	6.61	2.71	× 10^{-2}	11.8	0.401	0.078	2.88
8	15	6.61	2.71	× 10^{-2}	11.3	0.419	0.082	3.0
17	25	6.30	2.15	× 10^{-2}	5.2	0.915	0.178	8.3
9	25	6.30	2.15	× 10^{-2}	5.4	0.880	0.171	7.95
11	0	6.92	2.58	× 10^{-2}	73	0.072	0.0139	0.54 $[NaNO_3] = 5.0 \times 10^{-1}$
12	0	6.96	2.76	× 10^{-2}	3.6	1.32	0.257	9.3 $[Ox^{2-}] = 1 \times 10^{-2}$
13	0	7.12	4.07	× 10^{-2}	6.7	0.710	0.138	3.4 $[MeAO] = 2.4 \times 10^{-2}$
14	0	6.98	2.94	× 10^{-2}	15.9	0.300	0.0581	1.98 $[NH_4] = 1 \times 10^{-2}$

* $[PtBr_6]^{-2}$ (as precipitating agent)
† $[Ligand]_T$ initial = 5.13 × 10^{-3} mole/l
‡ Complex recrystallized 3× (25 per cent recovery)
§ Ligand recrystallized from (Acetone–MeOH)

a slight enhancement. Oxalate ion and MeAO increase the rate drastically even at relatively low concentrations (0.01 and 0.024 M respectively).

Since the evaluation of k_2' is dependent on knowing the free AO concentration it was necessary to determine the temperature dependence of the acid-dissociation constant of AOH in order to determine the temperature dependence of k_2'. Using a previously described method,[11] the values found were $pK_a = 9.82$, 9.49, 9.28 at 2°, 15° and 25° respectively giving a $-\Delta H$ of 8.04 kcal/mole at $\mu = 0.022$. Using runs 5, 7 and 9 and the dissociation constants of AOH^-, the free AO was found to be 3.56×10^{-5}, 2.71×10^{-5} and 2.15×10^{-5} M respectively which gave the k_2' values listed in Table 1. A graph of $\ln k_2'$ versus $1/T^0$A gave a nearly straight line with a slope corresponding to an E_a for ligand exchange of 13.8 kcal/mole. The rate of exchange follows the expression $k_2' = 1.8 \times 10^{12} \exp(-13{,}800/RT)$ l mole^{-1}, sec^{-1}.

$[Ni(MeAO^*)_2-H]^+ + 2MeAO \rightleftharpoons [Ni(MeAO)_2-H]^+ + 2MeAO^*$. This exchange is considerably slower than that of $[Ni(AO)_2-H]^+$ and thus the rates are more precise. No zero time exchange was found except at pH's below 7.5 where partial dissociation of the complex occurs. Fig. 2 shows the $[H^+]$ dependence of the pseudo first order rate constant at constant $[MeAO]_T$ defined in: Overall rate,

$$R = k[Ni(MeAO)_2-H^+]_T$$

Fig. 3 gives the *free* ligand dependence of the pseudo first order rate constant at a

---

[11] F. BASOLO and R. K. MURMANN, *J. Amer. Chem. Soc.* 74, 2373 (1952).

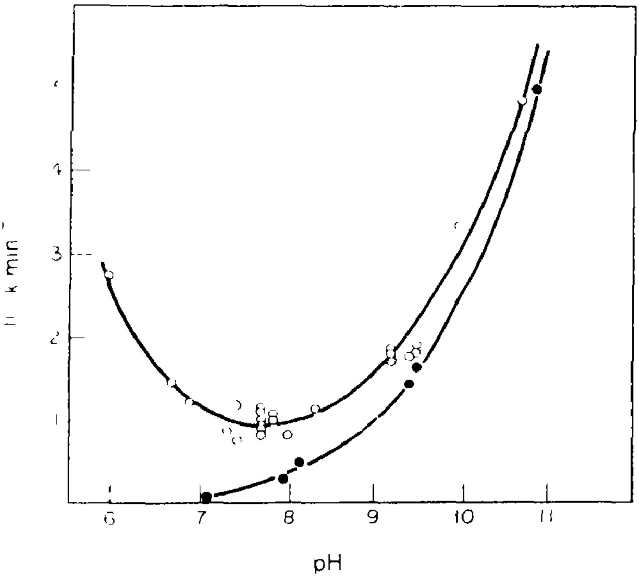


FIG 2 Rate Constant of Ligand Exchange, k vs pH 25 1 C
○ $[\mathrm{Ni(MeAO)_2\ H}]_T^+$ 1 0 10^{2} mole/l $[\mathrm{MeAO}]_f$ 2 5 10^{2} mole/l
● $[\mathrm{Ni(EnAO)\ H}]_T^+$ 3 9 10^{3} mole/l $[\mathrm{EnAO}]_f$ 4 0 10^{3} mole/l

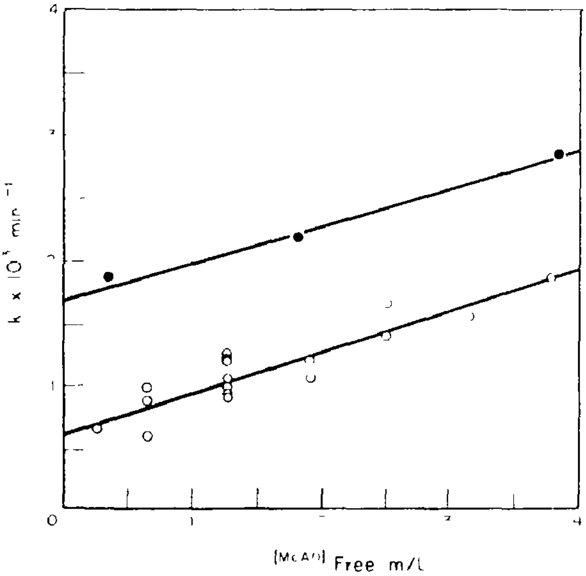


FIG 3 -- Rate Constant of Ligand Exchange for $[\mathrm{Ni(MeAO)_2{-}H}]^+$, 25 1C°
○ pH -- 7 7, $[\mathrm{MeAO}]_F \times 10^3$
● pH 9 5, $[\mathrm{MeAO}]_F$ 10^2 pk_a for MeAO = 8 98

J. Inorg. Nucl. Chem. 1963. Vol. 25, pp. 129 to 135. Pergamon Press Ltd. Printed in Northern Ireland

NOTES

The adsorption of di-n-butylphosphate from organic solutions on some metal oxides

(*Received* 6 *April* 1962, *in revised form* 19 *May* 1962)

IN THE course of certain experiments on the purification of degraded tributylphosphate-kerosene solutions, we noticed that di-n-butylphosphate (DBP) is easily adsorbed on Al_2O_3, ZrO_2, SiO_2, MnO_2 and probably on some other oxides. The adsorption processes were studied in more detail on the first three oxides, whereas granular MnO_2, owing to some inconvenient mechanical properties, was discarded.

Experimental

The following oxides, dried at 105°C to constant weight, were used: Merck's alumina "according to Brockmann" (100–150 mesh), Merck's silica-gel "for chromatography" (100–200 mesh) and hydrous zirconium oxide (100–150 mesh). Di-n-butylphosphate (purity 99%) was prepared according to KENNETH DUKES[1] and WAGNER.[2] Tributylphosphate (TBP) and kerosene were used as solvents.

In all cases, 25 ml of the DBP solution (in kerosene or in a mixture of 30 vol % TBP-kerosene) was shaken for 17 hr at 20 ± 2°C. The amount of DBP adsorbed was calculated from the decrease of its concentration in the solution.

Results and discussion

The adsorption isotherms (in pure kerosene solutions) have the same shape for all three adsorbents and they can be expressed fairly well by means of a Langmuir-type equation. In the range 40–100% of saturation the following equation was found to be valid:

$$K = q/[c(Q - q)] \qquad (1)$$

Here q is the adsorbed amount of DBP per 1 g of the adsorbent, Q is the same quantity at saturation, c is the equilibrium concentration of DBP in the solution (mmol/ml) and K is the equilibrium constant (ml mmol^{-1}). The values K and Q for the three adsorbents are given in the second and the third column of Table 1, respectively, whereas Fig. 1 shows the isotherms. The curves are calculated for the K- and Q-values given in Table 1, whereas the dots are the experimental results.

TABLE 1

Adsorbent	Kerosene		30% TBP-kerosene	30% TBP-0.1 M HNO_3-kerosene
	K* (ml mmol^{-1})	Q (mmol g^{-1})	Q' (mmol g^{-1})	Q (mmol g^{-1})
Al_2O_3	2.1×10^3	0.70	0.50	0.85
ZrO_2	1.4×10^3	1.10	0.80	0.76
SiO_2	3.4×10^1	0.65	0.01	0.01

* The ratio liquid: solid phase was 25 ml/g.

DBP is adsorbed on Al_2O_3 and ZrO_2 from TBP-kerosene solutions even if these solutions contain nitric acid. Some adsorption capacities in such solutions are given in the last two columns of Table 1. However, as it can be seen from the same table, DBP is not adsorbed on SiO_2 in the presence of large amounts of TBP. In that case, the adsorption is not specific and TBP removes DBP from SiO_2. In the case of Al_2O_3 and ZrO_2, however, there are many reasons for the assumption that a strong chemisorption takes place. For instance, it is well-known that these oxides firmly bind phosphate ions from aqueous solutions.

---

[1] E. KENNETH DUKES, TID-4500 (1957).
[2] R. M. WAGNER, HW-19959 (1951).

TABLE 2 EXCHANGE RATE CATALYSIS† $[Ni(MeAO)_2-H]^+$

pH	Catalyst	[Catalyst] × 10^2	$k \times 10^3$ min^{-1}
7.7	none	0.000	1.30
7.7	NH_3	0.65 × 10^{-3}	1.32
7.7	Ethylenediamine‡	0.27 × 10^{-3}	35.4
	EthylenediamineH	0.241	
7.7	N,N′-dimethylethylenediamine	0.64 × 10^{-4}	2.11
	(N,N′-dimethylethylenediamineH)	0.235	
7.7	N,N,N′,N′-tetramethylethylenediamine	0.0201	1.68
	(N,N,N′,N′-tetramethylethylenediamineH)	0.375	
9.5	Ethylenediamine	0.026	220
	(EthylenediamineH)	0.373	
8.5	Oxalate $^{2-}$	1.0	38.8

† $[Ni(MeAO)_2-H^+]_T$ = 1.0 × 10^{-2} mole/l, $[MeAO]_T$ = 5.0 × 10^{-2} mole/l, Temp = 25.1°C

‡ The concentrations of the forms of the catalysis were based on these acid-dissociation constants ethylenediamine, pK_1 = 7.52, pK_2 = 10.65, N,N′-dimethylethylenediamine, pK_1 = 7.47, pK_2 = 10.29, N,N,N′,N′-tetramethylethylenediamine, pK_1 = 5.85, pK_2 = 8.97

constant pH of 7.7 and 9.5. The scatter at 7.7 is partially due to the fact that the earlier experiments were not as precise and the errors are more obvious because of the expanded scale caused by the small $[MeAO]_F$ dependence. It is quite certain, however, that k is slightly ligand dependent. The values, for k_1 and k_2 obtained from this graph are pH = 7.7, k_1 = 6.2 × 10^{-4} min^{-1}, k_2 = 0.331 mole^{-1} min^{-1}, pH = 9.5, k_1 = 16.8 × 10^{-4} min^{-1}, k_2 = 0.031 mole^{-1} min^{-1}. Table 2 presents the effect of foreign ions and molecules on the rate of exchange. NH_3 and N,N,N′,N′-tetramethylethylenediamine have almost no effect while a small positive catalysis is noted by N,N′-dimethylethylenediamine. Ethylenediamine is an extremely effective catalyst while oxalate ion at the same concentration is less so.

Since the pseudo first order rate constant is only slightly MeAO dependent at pH = 7.7 its temperature dependence was evaluated without correction for the changes of the pK_a of $MeAOH^+$ with temperature. A graph of ln k vs $1/T$ was nearly linear giving a value for E_a of +16.6 kcal/mole for the ligand exchange of $[Ni(MeAO)_2-H]^+$. At pH = 7.7, $[Ni(MeAO)_2-H^+]_T$ = 1.0 × 10^{-2} M, $[MeAO]_T$ = 2.5 × 10^{-2} M, the reaction follows the law k = 2.3 × 10^7 exp(−16,600/RT) l mole^{-1} sec^{-1}.

$[Ni(EnAO^*)-H]^+ + EnAO \rightarrow [Ni(EnAO)-H]^+ + EnAO^*$. Figure 2 contains a graph of the $[H^+]$ dependence of the pseudo first order rate constant calculated from the expression $R = k[Ni(EnAO)-H^+]_T$. Experiments to determine the ligand dependence indicate that at least two isomeric forms of the ligand are present and that at least one does not participate in the exchange. This was previously suggested from a study of the kinetics of formation of the complex.(9a) On the basis of the fraction of free EnAO that does participate in the exchange, as shown by isotopic dilution, the ligand dependence appears quite small. Separation of the isomers of EnAO and subsequent determination of the ligand dependence is being undertaken.

$[Ni(AO)_2-H]^+ + Ni^{*2+} \rightleftarrows [Ni^*(AO)_2-H]^+ + Ni^{2+}$. The results of metal ion exchange with $[Ni(AO)_2-H]^+$ are presented in Fig. 5. The rate constant, k, was evaluated using the expression $R = k_M[Ni(AO)_2-H^+]_T$ and it appears to be Ni^{2+} independent at a pH of 7.2. The rate constant obtained by counting the precipitated complex, $[Ni(AO)_2—H]^+[Cr(NH_3)_2(SCN)_4]^-$, was identical with that obtained by measuring the activity decrease of the Ni^{2+} by precipitation with dimethylglyoxime

Using $[Ni(EnAO)—H]^+$ at a pH of 6 9 and following the activity of Ni^{2+} and of $[Ni(EnAO)—H]^+$, the half time was so slow it could not be measured An upper limit for the rate constant was evaluated, however, ($k_M = 2 \times 10^{-7}$ min^{-1})

The individual stepwise formation constants of the complexes are not well established and it is not possible to estimate the per cent concentrations of the complex species over a long pH range Since the rate of ligand and metal ion exchange depends on the amounts of each exchanging species some measure of the relative amounts of complex species as a function of pH was needed For this purpose pH titration curves were determined and are given in Fig 4 From these and the dissociation constants of the amines it can be seen that the formation constants are in the order $[Ni(EnAO)—H]$ $[Ni(AO)_2—H]^+$ $[Ni(MeAO)_2—H]^+$ and that the hydrogen bond in $[Ni(MeAO)_2—H]^+$ is considerably weaker thermodynamically than the others

DISCUSSION

The overall exchange reaction $[Ni(XX^*)_2—H]^+ + 2XX \rightleftharpoons [Ni(XX)_2—H]^+ + 2XX^*$, where XX = AO, MeAO proceeds by a two step process as described by equation 1

$$R = k_1[Ni(XX)_2—H^+]_F + k_2[Ni(XX)_2—H^+]_F[XX]_F$$

Proof of this process is shown by the graph of the pseudo first order rate constant, k, vs $[XX]_{Free}$ which, for the MeAO system, Fig 3, is a straight line with a positive slope The magnitude of the overall rate, R, for the three complexes studied is primarily determined by the value of k_2 since k_1 is relatively small Thus, $[Ni(AO)_2—H]$ is approximately 400 times faster exchanging than the corresponding MeAO or EnAO complexes because k_2 is extremely large This is illustrated by the fact that the k_1 term is not even observed in the AO system

Ligand dependence

The form of the rate expression suggests the same mechanism for ligand exchange on nickel (II) as that postulated by Basolo and Pearson⁽²⁾ for platinum (II), palladium (II) and nickel (II) replacement reactions The term involving k_1 may be visualized as being due to dissociation or displacement of the ligand by water molecules weakly held in the fifth and sixth positions while the second order term strongly suggests that in the activated state the free ligand occupies one of these positions and assists in the dissociation of the coordinated ligand

The relative magnitude of k_2 with different ligands is readily understood on the basis of steric hindrance which occurs only in the MeAO and EnAO systems In the MeAO complex, it is expected that the favored postion of the N-methyl groups will be toward opposite sides of the complex plane in order to reduce internal strain Models suggest that the 5 and 6 positions are partially blocked by co-ordinated ligand-N-methyl groups and prevent the close approach of bulky reactant molecules When the reactant is the N-methylamino group, (as in ligand exchange), strong repulsive forces between the methyl group of the reactant molecule and the methyl groups of the complex make the formation of the activated state unfavourable unless reorientation of the co-ordinated ligand methyl groups takes place Models indicate that water

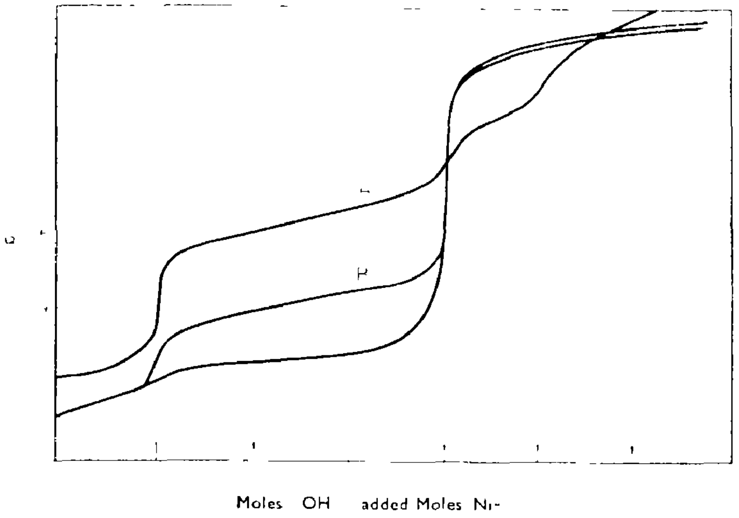


Fig 4 Titration curves *A* MeAO, *B* AO, *C* EnAO Ligand/Ni^{2} 2 except with EnAO when it was 1 T 25 1°C Zero on abscissa corresponds to a mixture of Ni^{2} and 2 Ligand H

AO and similar molecules would not be sterically hindered in their approach and, other factors being constant, could be effectively associated In the exchange of AO with $[Ni(AO)_2—H]^+$, neither the complex nor the entering ligand provides effective steric hindrance and thus k_2 is especially large Interpretation of the EnAO system is more difficult and it appears that steric hindrance due to the secondary amine nitrogen in the approaching ligand although important, is not the only factor Since catalysis by chelating ligands containing primary amines (i e en) is smaller by comparison with the AO and MeAO systems, it is suggested that more than one of the reaction steps following association is slow In order to speed up these steps multidentate ligands such as EDTA or EnAO are necessary

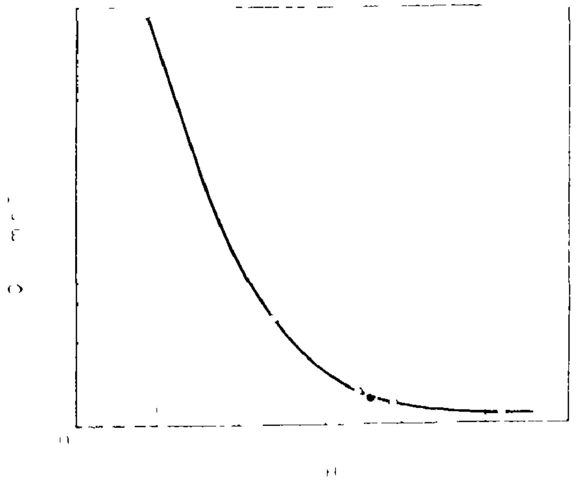


Fig 5 $[Ni(AO)_2$ H) Rate of Ni^{2+} exchange Rate k_H[Complex]$_T$ 25 3 C NH_4OAc - HOAc buffered

[Ni]^2 5 0 10 m/l ● [Ni] 1 0 10 mole/l

These results parallel those found in the reaction of the same complexes with EDTA(9b) where the kinetics follow the rate law $R = k_1[\text{complex}] + k_2[\text{complex}][\text{EDTA}]$ The EDTA dependent term increases in the order EnAO ≈ MeAO > AO which is expected if the EDTA molecule ion associates either through an amine nitrogen or a carboxyl oxygen

The determination of an exact value for k_1 is not possible from the data but further experiments on metal ion exchange (in progress) may give more precise information In the AO system the rates are determined by the large value of k_2 and k_1 cannot be evaluated Isotopic metal ion exchange data is more suitable for k_1 determination since excess ligand need not be present and the rate due to k_2 becomes vanishingly small Some preliminary results are described later The MeAO system presents a more favourable situation but another complication is present Fig 3 shows that at two pH's the pseudo first order rate constant does not extrapolate to the same value at $[\text{MeAO}]_f = 0$ The reason for this is that the exchange is not being carried by a single complex but by a pH dependent equilibrium mixture Fig 6 shows these equilibria for which only approximate equilibrium constants are known At pH = 7 7 and [MeAO] → 0 the exchange is carried predominately by $[\text{Ni(MeAO)}_2\text{—H}]$ while at pH = 9 5 and [MeAO] → 0, a moderate fraction is carried by

$$[\text{Ni(MeAO)}_2\text{—H(OH)}]^0$$

which apparently dissociates more rapidly The slope (Fig 3) decreases with increasing pH reflecting a decreased ligand dependent path due to the difficulty in replacing an OH^- group already present in the 5th position

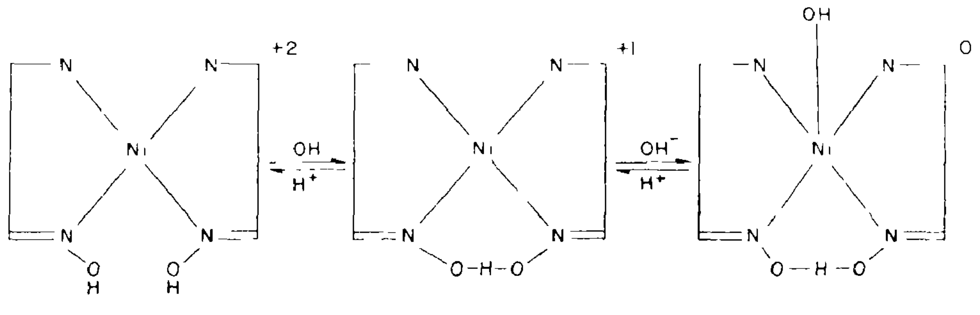


Fig. 6 —Complex equilibria

Acid dependence

AO The acid dependence of the ligand exchange of $[\text{Ni(AO)}_2\text{—H}]^+$ appears to be small in the pH range 6 3–9 4 as shown by the relative consistent values of k_2 in Table 1 The titration curve *B* in Fig 4 shows that in this pH region, the metal ion is almost entirely in the form, $[\text{Ni(AO)}_2\text{—H}]^+$. On this basis a small hydrogen ion dependence is expected in agreement with experiment

MeAO The pH dependence of the rate constant of ligand exchange of $[\text{Ni(MeAO)}_2\text{—H}]^+$ is large (Fig 2) The rapid rise in rate constant in the alkaline region is due to two effects

(a) Increased free ligand concentration (and thereby the rate due to the second order term) with increasing $[\text{OH}^-]$

(b) The contribution of $[Ni(MeAO)_2—H(OH)]^0$ at high pH's. The contribution of these two factors can be shown by Fig. 7.

When the overall rate, R, is converted into a pseudo k_2' a relatively constant value is obtained above a pH of 8.2. In this region the k_1 term is rather small and constant and may be neglected and the constancy of k_2' suggests that the rise in k in the alkaline region (Fig. 2) is primarily due to the increased free ligand concentration produced by increased base. The slight rise in k_2' around pH = 10.5 is just outside experimental

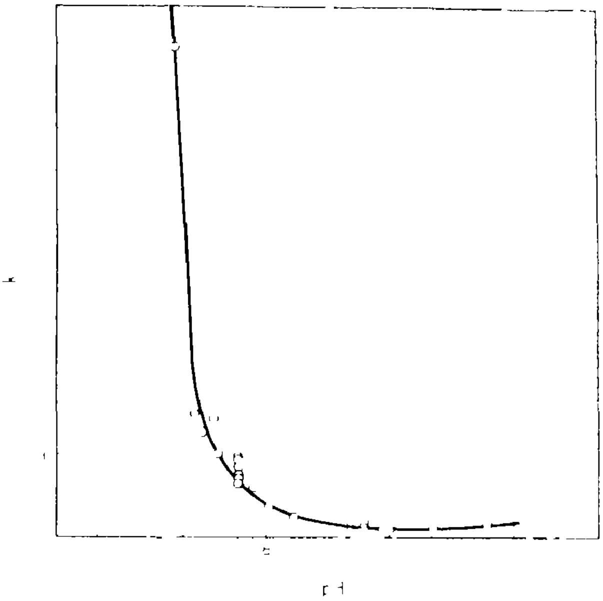


FIG. 7. k_2 vs pH for the ligand exchange of $[Ni(MeAO)_2—H]$
$k_2 = R/[Complex]_T [Ligand]_F$

error and may be due to a larger k_1 value for $[Ni(MeAO)_2—H(OH)]^0$ which is present in this alkaline region.

Below pH = 8, Fig. 2 shows that k increases with increasing acidity. Spectral and formation constant studies (to be published) indicate an extremely small concentration of $[Ni(MeAO)_2(H_2O)_2]^{2+}$ in the pH range 5.5–8.0 suggesting that it is not responsible for this effect unless it has an extremely fast reaction rate. On the basis of its similar spectra with the n-PrAO and n-AmAO complexes it is octahedral and should behave like $[Ni(en)_2(H_2O)_2]^{2+}$. The rate constant of ligand exchange for this complex has been estimated$^{(12b)}$ to be, $\log k_d = 0.72 \text{ sec}^{-1}$. If a value of the same order of magnitude is selected for $[Ni(MeAO)_2(H_2O)_2]^{2+}$, and taking into account its estimated concentration, the rate observed is considerably faster than that calculated. This suggests that the equilibrium formation of $[Ni(MeAO)_2(H_2O)_2]^{2+}$ is not responsible for most of the increased rate and an appealing explanation rests with a half-bonded intermediate suggested by POPPLEWELL and WILKINS for $[Ni(Tetrameen)_2]^{2+}$.$^{(12a)}$ A dissociated amine group may either reattach or complete the dissociation of the ligand by rupture of the other bond. Increasing the acidity would cause increased

---

(12) a D. S. POPPLEWELL and R. G. WILKINS *J. Chem. Soc.* 4098 (1955).
b A. K. SHAMSUDDIN AHMED and R. G. WILKINS *J. Chem. Soc.* 2901 (1960).

association of the uncomplexed amine group with H$^+$ and prevent reattachment thus facilitating the dissociation and exchange This half-bonded mechanism has been proposed for other Fe(II) and Ni(II) complex reactions and may be responsible for the increased rate of exchange in the acid region

EnAO That there is no increase in rate constant, k, (Fig 2) in the acidic region is consistant with the half-bonded mechanism since the presence of the ethylene bridge between the two nitrogens prevents their independent dissociation Since the ligand dependence for the EnAO complex is small, it appears that the large increase in k in the alkaline region is not primarily due to ligand association at the fifth position This suggests that OH modifies the complex either by direct association at the fifth position or by breaking the hydrogen bond This is discussed under metal ion exchange

Temperature dependence

The activation energy of the exchange reaction, E_a, is clearly higher for [Ni(MeAO)$_2$ H] (16 6 kcal/mole) than for [Ni(AO)$_2$ H]$^+$ (13 8 kcal/mole) This is in agreement with the mechanism proposed since the former is carried primarily by the k_1 rate term and the latter by the k_2 term If we consider the k_1 rate term to be a dissociation facilitated by water molecules in the *trans* position and the k_2 dissociation facilitated by an AO molecule attached through an amine nitrogen in a *trans* position, and the distortion of the planar state to be larger with the stronger associating ligand (AO) then the energy necessary to reach the activated state would be less for the more highly distorted complex Thus the loss of C F S E upon association of [Ni(AO)$_2$—H]$^+$ with AO and water to give a distorted octahedral configuration weakens the AO Ni bonds in the plane more than does simple water association giving a lower activation energy

Catalysis of exchange

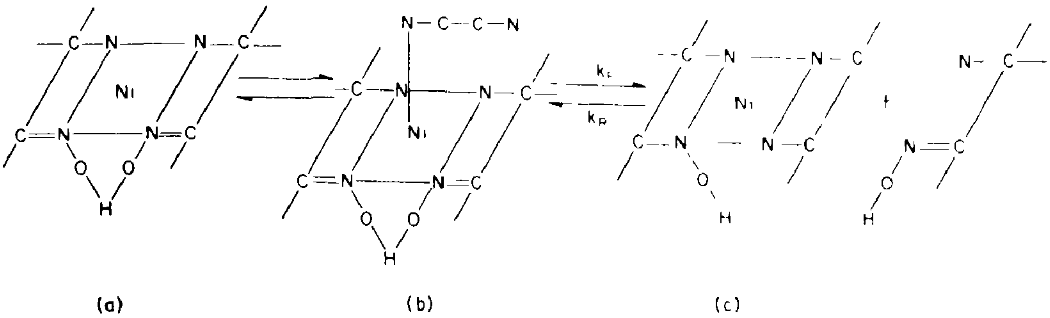
Table 1, runs (11 14), show that NO$_3^-$ lowers, NH$_3$ has little effect on, and oxalate ion and MeAO increase the rate of exchange of [Ni(AO)$_2$—H]$^+$ Identical results were obtained with [Ni(MeAO)$_2$—H] (Table 2) The lowering of the rate constant by NO$_3$ may be a salt effect but, more probably is due to association with the complex, effectively reducing the association of the exchanging ligand and thus lowering the rate constant The fact that NH$_3$ has little effect suggests that the associating ligand can only be effective in causing exchange if it has a second co-ordinating atom which can, (a) displace one of the original coordinated atoms or (b) co-ordinate with an open position left by a half dissociated ligand

Steric hindrance is important since substitution of one methyl group on each nitrogen of ethylenediamine makes it a much less effective catalyst and two methyl groups on each nitrogen prevents catalysis

Using a chelating group containing oxygen co-ordinating atoms, oxalate ion catalysis is observed but to a lesser extent In the cases studied, less than 1 per cent of the complex reacts to form a mixed complex at equilibrium

From the behaviour of ethylenediamine at two pH's the contribution of en and enH$^+$ were determined The ratio of effectiveness at unit activity is en/enH 4 6 $\times$ 10^3 This ratio is much larger than statistically expected but is of the correct order of magnitude for a simple inductive effect

Basing the inductive effect on the acid-base dissociation constants of ethylenediamine, ($pk_1 = 10.65$, $pk_2 = 7.52$) and assuming the associative tendency for the complex to be directly related to that for H^+, the ratio of the expected ability of en to enH^+ to coordinate can be estimated. After combination with the statistical factor of two, because of two positions in en versus one in enH^+, one obtains log $(en/enH^+) = 3.43$. This compares favourably with the experimental value of 3.66 suggesting that



an inductive effect is responsible for the difference in catalytic properties of en and enH^+.

The catalysis by foreign chelating ions may be explained by the above scheme using ethylenediamine as an example. Although the amounts of *b* and *c* are small at equilibrium k_F and k_R are large and the release of AO results in a rapid ligand exchange.

Metal ion exchange

The rate constant of Ni(II) ion exchange with $[Ni(AO)_2{-}H]$ decreases with increasing pH reaching a constant value of 7.3×10^{-4} min^{-1} at a pH of about 7.5. From the one observation made, it appears that the rate is nearly independent of $[Ni^{2+}]$ in the region of pH 7. Since formation constant studies have shown with a reasonable degree of certainty that the mono-complex has an extremely low stability, each time a ligand dissociates the other ligand also comes off. This suggests that $k_M = k_1 = 7.3 \times 10^{-4}$ min^{-1} for $[Ni(AO)_2{-}H]$ in a pH range 7.5–8.5. Increasing the acidity increases k_M in a manner similar to that found for ligand exchange with $[Ni(MeAO)_2{-}H]^-$. This adds further support to the postulated acid-dependence of the ligand exchange of $[Ni(MeAO)_2{-}H]^-$, namely a half-bonded intermediate interacting with $[H^+]_{aq}$.

With $[Ni(EnAO)_2{-}H]^+$ at a pH of 6.9 and 25.3, k_M is less than 2×10^{-7} min^{-1} and is much smaller than the ligand exchange measurements which have a value of k of about 1×10^{-4} min^{-1}. Since the ligand exchange rate has a small EnAO dependence, the activated state for ligand exchange probably involves a rate determining dissociation of two coordinating positions of the complex followed by a rapid addition of a second ligand to form a symmetrical complex containing 2-EnAO's. Exchange occurs upon reformation of the original complex. Alkaline conditions cause an increase in rate of ligand exchange and it is suggested that the two oxime groups become uncoordinated since this would be facilitated by OH^- addition to the complex (either by 5-position association or by breaking the hydrogen bond).

Table 3 gives estimates of the rate constants of dissociation of the complexes listed as derived from ligand and metal ion exchange. k_1 refers to the dissociation rate constant for that species alone without the contribution of mono or un-hydrogen bonded species.

TABLE 3. RATE CONSTANTS OF DISSOCIATION (25.3°C)

Complex	pH	k_1(min^{-1})
$[Ni(AO)_2-H]^+$	7.7–8.5	7.3×10^{-1}
$[Ni(MeAO)_2-H]^+$	7.7	6.2×10^{-4}
$[Ni(EnAO)-H]^+$	6.9	2×10^{-7}

It is apparent that N-methyl substitution has little effect while the dissociation constant for a similar tetradentate ligand is much smaller.

The results on ligand and metal ion exchange kinetics parallel those found with the EDTA reaction with the same complexes. The points of similarity are

(a) relative order of the rate constants with different complexes,

(b) a two term rate law containing a reactant independent and a reactant dependent term,

(c) catalysis by foreign chelating ions,

(d) a minimum in rate constants in the region of stability of the hydrogen bond and

(e) catalysis by hydrogen ion in acidic regions.

Thus these studies support the associative mechanism proposed for the reaction of planar nickel (II) complexes with EDTA and suggest that other planar nickel (II) reactions will follow similar paths.

SUMMARY

The rates of ligand exchange of three planar nickel (II) ions follow the rate law rate = $k_1[\text{complex}]_T + k_2[\text{complex}]_T[\text{ligand}]_T$. k_1 is relatively small and thus k_2 determines the overall rate. The value of $k_1 + k_2$ is AO MeAO EnAO. The activation energy for the k_2 term is small compared to that for k_1. Below a pH of 6 the rate is acid dependent and this is interpreted on the basis of a half-bonded intermediate which can either re-coordinate or associate with an $[H^+]_{aq}$. The exchange rates are strongly catalysed by foreign chelating agents such as oxalate ion or ethylenediamine due to the rapid rate of formation of the mixed ligand complex. The metal ion exchange rates show a behaviour compatible with the ligand exchange interpretation.

Based on these experiments and the similarity of the results with those found for the reaction of planar Ni(II) ions with EDTA, an intermediate for both reactions is postulated with the reactant molecule coordinated in the fifth position in the activated state.

J. Inorg. Nucl. Chem. 1963. Vol. 25, pp. 1445 to 1455. Pergamon Press Ltd. Printed in Northern Ireland

RATE LAWS FOR THE U(IV)-U(VI) EXCHANGE REACTION IN AQUEOUS-ORGANIC MIXED SOLVENT SYSTEMS*

J. O. WEAR
Sandia Laboratory, Albuquerque, New Mexico

(*Received* 17 *December* 1962; *in revised form* 10 *April* 1963)

Abstract—Rate laws have been written and discussed for the U(IV)–U(VI) exchange reaction in the following mixed solvents: 30, 60, 90 and 98 volume per cent ethanol–water; 30, 60, 90, and 98 volume per cent ethylene glycol–water; and 30, 60, and 90 volume per cent acetone–water.

THE exchange reaction between U(IV) and U(VI) has been studied by several authors in water and mixed solvents. The reaction has been studied in aqueous hydrochloric acid[1] and aqueous sulphuric acid solutions.[2] The reaction has also been studied in mixed aqueous hydrochloric acid–ethanol,[3] mixed aqueous hydrochloric acid–ethylene glycol,[4] and mixed aqueous hydrochloric acid–acetone media.[5]

The authors of these studies[1–5] have either presented no rate equations or have presented simple rate laws with the observed orders rounded off to integral values. Numerical comparisons of the observed reaction rates and these rate equations have not been carried out. In the present paper, an attempt has been made to write reasonable rate laws that will reproduce the observed rates of reaction.

The mixed solvent systems are presented in the following order: ethanol–water, ethylene glycol–water, and acetone–water.

Ethanol–water

MATHEWS *et al.*[3] studied the U(IV)–U(VI) electron exchange reaction in the following ethanol–water mixed solvents: 30, 60, 90 and 98† vol. per cent ethanol and their data are used in this discussion. Nonintegral orders were found in all the solvent mixtures and some of the orders could not be made integral within the limits of the experimental error, which was ±10 per cent.[6] The orders and specific velocity constants are tabulated in Table 1 for each solvent.

MATHEWS *et al.*[3] wrote rate expressions for integral orders in 30 and 60 vol. per cent ethanol solvents, but they used the assumption that $[H^+]/K_1 \gg 1$ where $[H^+] \sim 1 \times 10^{-1}$ and K_1 [the U(IV) hydrolysis constant] is assumed to be about 2×10^{-2}

---

* Work performed under the auspices of the U.S. Atomic Energy Commission.

† Authors did not take into account the water in $UO_2Cl_2 \cdot H_2O$ and tracer solution.

[1] F. RONA, *J. Amer. Chem. Soc.* **72**, 4339 (1950); *Radioisotopes in Scientific Research* (Edited by R. C. EXTERMANN), Vol. 2, pp. 296–304. Pergamon Press, New York (1958).

[2] R. J. BETTS, *Canad. J. Res.* **26 B**, 702 (1948).

[3] D. M. MATHEWS, J. D. HEFLEY and E. S. AMIS, *J. Phys. Chem.*, **63**, 1236 (1959).

[4] S. L. MELTON, J. O. WEAR and E. S. AMIS, *J. Inorg. Nucl. Chem.* **17**, 317 (1961).

[5] S. L. MELTON, A. INDELLI and E. S. AMIS, *J. Inorg. Nucl. Chem.* **17**, 325 (1961).

[6] D. M. MATHEWS, Thesis, University of Arkansas (1959).

TABLE 1.—SPECIFIC RATE CONSTANTS AND ORDERS OF U(IV), U(VI), AND H^+ IN VARIOUS ETHANOL–WATER SOLVENT MIXTURES

Vol % EtOH	U(IV) order	U(VI) order	H^+ order	$k' \times 10^2$
0*	2.0	1.0	3.0	0.056 or 0.086
30	0.93	1.11	1.74	0.445
60	0.87	1.08	0.97	11.6
90	2.89	0.10	1.06	2328
98	0.0	2.70	1.26	167

* From reference (1).

In the following discussion rate laws are proposed for the U(IV)–U(VI) exchange reaction in the 30, 60, 90, and 98 vol per cent ethanol–water solvents and discussed in view of the experimental data.

In the 30 vol per cent ethanol solvent the following rate expression can be written

$$R = k_1[UOH^{3+}][UO_2OH^+] \qquad (1)$$

Where $[UOH^{3+}]$ and $[UO_2OH^+]$ can be determined from the following equilibrium constants

$$K_1 = \frac{[UOH^{3+}][H^+]}{[U^{4+}]} \qquad (2)$$

$$K_2 = \frac{[UO_2OH^+][H^+]}{[UO_2^{2+}]} \qquad (3)$$

where $K_1 = 2.4 \times 10^{-2}$[7] and $K_2 = 9.6 \times 10^{-6}$[3]. Solving Equations (2) and (3) for $[UOH^{3+}]$ and $[UO_2OH^+]$ and substituting into equation (1) with the assumption $[H^+] \gg K_2$ the following rate law is obtained

$$R = \frac{k_1'[U(IV)][U(VI)]}{[H^+]([H^+] + K_1)} \qquad (4)$$

where $k_1' = k_1K_1K_2$.

The apparent specific velocity constant, k_1', was calculated to be 2.37×10^{-3} moles l^{-1} min^{-1} from the experimental data. The rates calculated with this value of k_1' and the concentration of the reactants are tabulated in Table 2. In the last column of Table 2 is shown the per cent that R_{calc} deviates from R_{obs}.

In the 60 vol per cent ethanol solvent the same hydrolyses (Equations 2 and 3) are considered to be important and K_1 and K_2 are 1.4×10^{-2} and 5.2 × 10 [illegible] respectively.

A reasonable rate expression can be written by adding a term to the rate expression for 30 vol per cent ethanol solvent as follows

$$R = k_1[UOH^{3+}][UO_2OH^+] + k_2[U^{4+}][UO_2^{2+}] \qquad (5)$$

Again solving Equations (2) and (3) for the ionic concentrations in terms of [U(I

---

(7) K. A. KRAUS and F. NELSON, Report ORNL-496 (1950).

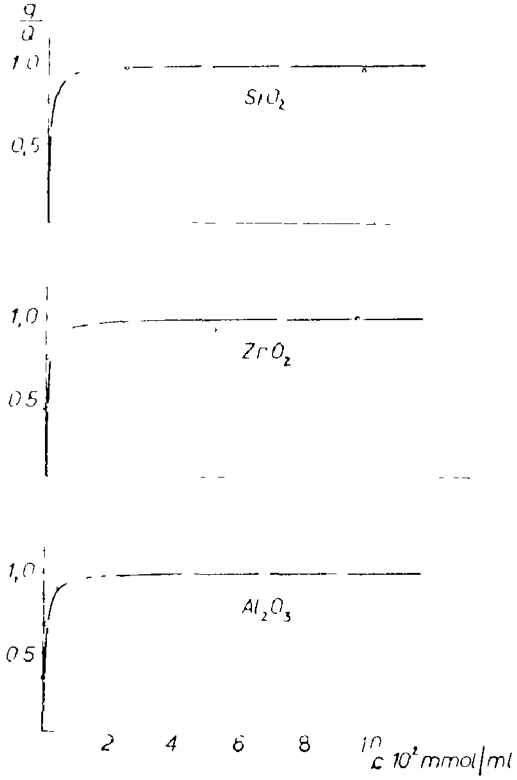


FIG. 1. Adsorption isotherms (kerosene solution). The curves represent equation (1) for the K- and Q values in Table 1, the dots are the experimental results.

The adsorption of DBP on these oxides might be useful in the cleaning procedure of some degraded solvents. We succeeded in removing quantitatively DBP from organic solvents by passing them through a column filled with Al_2O_3. Some difficulties arose in removing DBP from the column. Up to the present, the best results were obtained by washing the column with a weakly alkaline saturated aqueous solution of Na_2SO_4. A more detailed investigation of the adsorption of DBP on Al_2O_3 is in progress.

Institute of Nuclear Sciences
Boris Kidrich
Belgrade, Yugoslavia

I. J. GAL
DJ. M. PETKOVIC

The U.V. spectrum of aqueous BrCl

(*Received* 8 *June* 1962)

THE NEAR U.V. spectrum of bromine chloride in carbon tetrachloride is well known, both the wavelength and extinction coefficient of the absorption maximum lying between the values for bromine and chlorine⁽¹⁾. PUNGOR, BURGER and SCHULEK⁽²⁾ have measured the absorption due to BrCl in aqueous solution and find an absorption maximum at 343 mμ: the so called *L* values given in these authors' diagrams do not appear to be self-consistent and cannot be extinction coefficients as suggested in the text.

The hydrolysis of bromine is largely suppressed in 2N perchloric acid solution but chlorine hydrolyses appreciably in this acid unless chloride ions are present. We have measured the spectrum of BrCl in 2N perchloric acid solution in the presence of excess bromine. This procedure has several

---

(1) A. I. POPOV and J. J. MANNION, *J. Amer. Chem. Soc.* **74,** 222 (1952).

(2) E. PUNGOR, K. BURGER and E. SCHULEK, *J. Inorg. Nucl. Chem.* **11,** 56 (1959).

TABLE 2.—A COMPARISON OF THE OBSERVED AND CALCULATED INITIAL RATES FOR THE U(IV)–U(VI) EXCHANGE REACTION IN WATER–ETHANOL MIXED SOLVENTS AT 25°C

[U(IV)] 10^2 (M)	[U(VI)] 10^2 (M)	$[H^+]$ 10^2 (M)	R_{obs} 10 (M min^{-1})	R_{calc} 10 (M min^{-1})	Deviation (%)
		30% Ethanol			
1.90	1.89	13.02	4.29	4.24	1.2
0.95	1.47	3.26	19.0	17.9	5.8
2.85	2.30	3.26	88.2	84.3	4.4
1.90	2.94	3.26	61.4	71.7	16.8
1.90	4.00	6.51	33.1	31.0	6.3
1.90	1.89	3.26	46.9	46.1	1.7
1.90	1.89	6.51	14.0	14.7	5.0
					Ave 5.9
		60% Ethanol			
1.90	2.94	3.23	167.0	175.0	4.8
1.90	2.94	6.51	75.5	71.6	5.2
1.90	2.94	13.02	44.2	42.6	3.6
1.90	1.89	13.02	28.6	27.4	4.2
0.95	2.53	13.02	19.5	18.3	6.6
2.85	3.36	13.02	68.9	73.0	6.0
1.90	4.00	13.02	65.2	58.0	11.0
					Ave 5.9
		90% Ethanol			
1.68	2.11	18.65	72.0	82.3	14.3
1.68	2.11	25.16	51.9	54.4	4.8
1.68	2.11	31.45	41.0	44.3	8.0
1.68	1.15	25.16	50.9	47.4	6.9
1.68	1.58	25.16	54.8	50.5	8.5
0.79	1.64	25.16	9.8	9.7	1.0
2.37	2.80	25.16	144.0	143.0	0.7
1.68	2.16	25.16	56.3	54.8	2.7
					Ave 5.9
		98% Ethanol			
1.32	1.41	3.86	118.0	127.0	7.6
1.32	1.41	7.71	41.8	42.3	1.2
1.32	1.41	11.57	27.8	26.7	4.0
1.32	2.09	7.71	119.0	110.0	7.6
1.32	2.77	7.71	248.0	235.0	5.2
2.02	2.08	7.71	106.0	102.0	3.8
					Ave 4.9

[U(VI)] and $[H^+]$ and substituting into equation (5) with the assumption $[H^+] \quad K_2$, the following equation is obtained

$$R = \frac{k_1'[U(IV)][U(VI)]}{[H^+]([H^+] + K_1)} + \frac{k_2[U(IV)][U(VI)][H^+]}{K_1 + [H^+]} \tag{6}$$

where $k_1' = k_1K_1K_2$.

Graphically k_1' and k_2 were found to be 5.86 × 10^{-3} moles l^{-1} min^{-1} and 0.740 l mole^{-1} min^{-1}, respectively. The rates calculated with these values of k_1' and k_2 are tabulated in Table 2. The average deviation of R_{calc} from R_{obs} is + 5.9 per cent

As the ethanol content is increased to 90 vol per cent the rate increases by 200 fold as can be seen in Table 1. This radical change in rate as well as a shift in orders indicates a very different reaction path.

The U(IV) hydrolysis is still important, but K_1 is now 3.4×10^{-3}. A new equilibrium express by the following equilibrium constant is introduced

$$K_3 = \frac{[\mathrm{UOOH}^{3+}]}{[\mathrm{UO}_2^{2+}][\mathrm{H}^+]} \tag{7}$$

For 90 vol per cent ethanol solvent the following rate law can be written

$$R = k_1[\mathrm{U}^{4+}][\mathrm{UOH}^{3+}]^2 + k_2[\mathrm{UOOH}^{3+}][\mathrm{U}^{4+}] \tag{8}$$

With the aid of Equations (2) and (7) and assuming $K_1 \ll [\mathrm{H}^+]$ and $K_3[\mathrm{H}^+] \ll 1$ the following rate expression is obtained

$$R = \frac{k_1'[\mathrm{U(IV)}]^3}{[\mathrm{H}^+]^2} + k_2'[\mathrm{H}^+][\mathrm{U(VI)}][\mathrm{U(IV)}] \tag{9}$$

where $k_1' = k_1K_1^2$ and $k_2' = k_2K_3$.

Graphically, k_1' and k_2' were found to be 5.20 min^{-1} and 1.74 $\mathrm{l}^2\ \mathrm{moles}^{-2}\ \mathrm{min}^{-1}$, respectively. Using these values for k_1' and k_2' the rates were calculated and are tabulated in Table 2. The average per cent deviation of R_{calc} from R_{obs} is ±5.9 per cent.

At 98 vol per cent ethanol, the specific velocity constant is a factor of 15 lower than it is 90 vol per cent ethanol. This possibly indicates the importance now of the two solvolyses with the following equilibrium constants

$$K_4 = \frac{[\mathrm{UO_2OEt}^+][\mathrm{H}^+]}{[\mathrm{UO}_2^{2+}]} \tag{10}$$

$$K_5 = \frac{[\mathrm{UOEt}^{3+}][\mathrm{H}^+]}{[\mathrm{U}^{4+}]} \tag{11}$$

Taking the above equilibria into account the following rate expression can be written

$$R = k_1'[\mathrm{UO_2OEt}^+]^2[\mathrm{UO}_2^{2+}] + k_2'[\mathrm{U_2O_2(OEt)_2}^{4+}] \tag{12}$$

$[\mathrm{U_2O_2(OEt)_2}^{4+}]$ can be found using the following two equilibria

$$K_6 = \frac{[\mathrm{U_2(OEt)_2}^{6+}]}{[\mathrm{UOEt}^{3+}]^2} \tag{13}$$

$$K_7 = \frac{[\mathrm{U_2O_2(OEt)_2}^{4+}][\mathrm{U}^{4+}]}{[\mathrm{U_2(OEt)_2}^{6+}][\mathrm{UO}_2^{2+}]} \tag{14}$$

With the use of Equations (10), (11), (13) and (14) and the assumption that K_4

$[H^+]$, $[U^{4+}] \approx [U(IV)]$, and $[UOEt^{3+}]$ is constant and small, Equation (12) becomes

$$R = \frac{k_1[U(VI)]^3}{[H^+]^2} + k_2\frac{[U(VI)]}{[U(IV)]} \tag{15}$$

where $k_1 = k_1' K_1^2$ and $k_2 = k_2' K_6 K_7 [UOEt^{3+}]^2$.

Graphically, k_1 and k_2 were determined to be 0.57 min^{-1} and 1.49×10^{-4} moles l^{-1} min^{-1}, respectively. Using these values of k_1 and k_2 the rates were calculated and are compared with the observed initial rates in Table 2, where it can be seen that the average deviation of R_{calc} from R_{obs} is ±4.9 per cent.

The rate laws proposed for the water–ethanol mixtures permit the changes in rate with increasing ethanol. Even the radical changes in rate and orders from 60 to 90 vol per cent ethanol are accounted for. The calculated rates are all within the experimental error of the observed rates. Polymeric ions at high ethanol content have been considered which are probable with a low dielectric.

Ethylene glycol–water

The U(IV)–U(VI) electron exchange reaction has been studied in 30, 60, 90 and 98* vol per cent ethylene glycol–water mixed solvents by MILLION, WEAR and AMIS(4), and their data are used in this discussion. The reported error in this study is also ±10 per cent. As in the ethanol–water system, non-integral orders were found. The orders and specific velocity constants are tabulated in Table 3 for each solvent.

TABLE 3.—SPECIFIC RATE CONSTANTS AND ORDERS OF U(IV), U(VI), AND H^+ IN VARIOUS ETHYLENE GLYCOL–WATER SOLVENT MIXTURE

Vol Ethylene glycol	U(IV) order	U(VI) order	H^+ order	$k \times 10^4$
30	0.75	0.68	1.35	0.218
60	0.95	0.91	1.14	1.47
90	1.35	0.79	0.24	135
98	0.66	0.85	0.53	3.05

In the discussion that follows, rate laws are proposed and discussed for the 30, 60, 90, and 98 vol per cent ethylene glycol–water solvents. The same assumptions are made on the values of K_1 and k_2 as were made in the ethanol–water discussion.

The experimental data in the 30 vol per cent ethylene glycol solvent can be reproduced by the rate expression for the 60 vol per cent ethanol solvent, i.e. Equation (6).

Graphically, k_1' and k_2 are determined to be 5.0×10^{-4} moles l^{-1} min^{-1} and 5.6×10^{-5} l $moles^{-1}$ min^{-1}, respectively. The rates have been calculated with these values of k_1' and k_2 and are tabulated for comparison in Table 4. The average deviation of R_{calc} from R_{obs} is ±8.9 per cent.

Changing the ethylene glycol composition to 60 vol per cent requires no change

---

* Authors did not take into account water in UO_2Cl_2 H_2O and tracer solution.

TABLE 4. A COMPARISON OF THE OBSERVED AND CALCULATED INITIAL RATES FOR THE U(IV)—U(VI) EXCHANGE REACTION IN WATER–ETHYLENE GLYCOL MIXED SOLVENTS AT 25°C

[U(IV)] 10^2 (M)	[U(VI)] 10^2 (M)	[H$^+$] (M)	R_{obs} 10^7 (M min^{-1})	R_{calc} 10^7 (M min^{-1})	Deviation (%)
		30% Ethylene glycol			
3.751	1.079	0.1216	13.40	14.49	8.1
3.751	1.079	0.2148	5.89	6.24	5.9
3.751	1.079	0.3544	3.49	3.59	2.9
1.896	1.344	0.1322	9.92	8.09	18.1
1.896	2.333	0.1323	14.56	14.05	3.5
1.896	3.323	0.1324	18.84	20.00	6.2
0.938	1.167	0.1654	3.43	2.44	28.9
3.792	1.699	0.1799	13.24	14.26	7.7
					Ave 8.9
		60% Ethylene glycol			
1.875	1.034	0.2619	2.65	2.65	0.0
1.875	1.034	0.1957	3.94	3.28	16.8
1.875	1.034	0.3354	2.02	2.34	15.8
0.938	1.012	0.1993	1.51	1.58	4.6
2.813	1.057	0.2105	4.11	4.74	15.3
3.751	1.079	0.2148	5.18	6.34	22.4
1.875	1.034	0.1173	6.54	5.75	12.1
1.875	1.034	0.1320	5.20	4.95	4.8
1.875	1.034	0.1516	5.27	4.22	19.9
1.875	1.034	0.1122	5.59	6.09	8.9
1.875	2.024	0.1123	10.81	11.92	10.3
1.875	3.013	0.1124	16.69	17.75	6.4
					Ave 11.4
		90% Ethylene glycol			
1.806	0.720	0.1269	7.62	7.75	1.7
1.806	0.720	0.1858	8.49	8.38	1.3
1.806	0.720	0.2646	9.29	9.49	2.2
1.806	1.395	0.1858	12.99	13.58	4.5
1.806	2.070	0.1858	18.57	18.69	0.6
1.806	2.746	0.1858	23.30	23.80	2.1
0.902	0.698	0.1965	3.09	3.46	12.0
2.708	0.742	0.2114	13.73	15.73	14.6
3.612	0.764	0.2189	23.12	24.59	6.4
					Ave 5.0
		98% Ethylene glycol			
1.815	0.723	0.1904	7.68	7.20	6.0
1.815	0.723	0.2694	6.36	6.03	5.2
1.815	0.723	0.1272	9.48	9.17	3.3
1.815	1.402	0.1272	16.02	17.78	11.0
1.815	2.081	0.1272	23.32	26.39	13.2
0.907	0.698	0.1215	6.08	6.11	0.5
2.722	0.742	0.1362	12.48	11.87	4.9
3.636	0.765	0.1436	14.59	14.58	0.1
					Ave 5.5

in the rate law. However, since the rate of the reaction increases it is necessary to determine different values for k_1' and k_2.

Graphically k_1' and k_2 were determined to be 3.23×10^{-5} moles l^{-1} min^{-1} and 9.70×10^{-4} l moles^{-1} min^{-1}, respectively. From these values of k_1' and k_2 the rates have been calculated and are tabulated in Table 4. The average deviation of R_{calc} from R_{obs} is ± 11.4 per cent.

When the ethylene glycol composition is increased to 90 vol per cent the order with respect to acid changes from negative to positive which indicates a major change in the mechanism. Also, the rate of the reaction increases about one hundred-fold. This increase in rate indicates that some much faster reaction paths have become important.

The following rate expression can be written

$$R = k_1[U^{4+}][UO_2^{2+}] + k_2[U^{4+}][UOOH^{3+}] + k_3[U^{4+}]^2 + k_4[UOH^{3+}][UOOH^{3+}] \tag{16}$$

By using Equations (2), (3) and (7) and making the assumptions that $K_1 \quad [H^+]$ and $K_3[H^+] \quad 1$ the following equation is obtained

$$R = k_1[U(IV)][U(VI)] + k_2'[U(IV)][U(VI)][H^+] + k_3[U(IV)]^2 + k_4'[U(IV)][U(VI)] \tag{17}$$

where $k_2' = k_2 K_1$ and $k_4' = k_4 K_1 K_3$.

Graphically, k_2', and k_3 and $k_1 + k_4'$ were determined to be 9.26×10^{-3} l^2 moles^{-2} min^{-1}, 9.27×10^{-1} l moles^{-1} min^{-1}, and 2.39×10^{-3} l mole^{-1} min^{-1}, respectively. Using these values of k_2', k_3 and $k_1 + k_4'$ the rates were calculated and are tabulated in Table 4. The average deviation of R_{calc} from R_{obs} is ± 5.0 per cent.

Again, from the 90 vol per cent organic solvent to the 98 vol per cent organic solvent, there is a sharp decrease in rate. Perhaps this sharp decrease is because of solvent taking part in a solvolysis.

The experimental data from the 98 vol per cent ethylene glycol can be accounted for by the following rate expressions

$$R = k_1[UO_2^{2+}] + k_2[UOCH_2\,CH_2OH^{3+}][UO_2^{2+}] \tag{18}$$

The species $[UOCH_2\,CH_2OH^{3+}]$ can be detemined from the following solvolysis constant

$$K_8 = \frac{[UOCH_2\,CH_2OH^{3+}][H^+]}{[U^{4+}]} \tag{19}$$

With Equation (19) and assuming $[UO_2^{2+}] \approx [U(VI)]$ and $K_8 \quad [H^+]$ the following rate law is obtained from equation (18)

$$R = k_1[U(VI)] + k_2'\frac{[U(IV)][U(VI)]}{[H^+]} \tag{20}$$

where $k_2' = k_2 K_8$.

Graphically, k_1 and k_2' were found to be 4.44×10^{-5} min^{-1} and 5.78×10^{-4} respectively. Using these values of k_1 and k_2' the rates have been calculated and are tabulated in Table 4. The average deviation of R_{calc} from R_{obs} is ± 5.5 per cent

The observation that the rates in ethylene glycol–water are slower than those in ethanol–water by two to four orders of magnitude is attributed to the chelation of the uranium ions by the ethylene glycol molecules. This chelation could create a tightly bound solvent shell around the ions and make exchange more difficult. Considering this chelation factor, the rate laws for the ethylene glycol system are not much different from those for the ethanol system.

Acetone–water

MELTON *et al.*[illegible] have studied the U(IV)–U(VI) electron exchange reaction in 30, 60, and 90 vol per cent acetone–water mixed solvents, and their data are used in this discussion. The orders were once again nonintegral as is shown in Table 5.

In the following discussion rate laws are proposed for the 30, 60, and 90 vol per cent acetone–water solvents. The same assumptions are made on the values of K_1 and K_2 as were made in the ethanol–water discussion.

TABLE 5 — SPECIFIC RATE CONSTANT AND ORDERS OF U(IV), U(VI), AND H^+ IN VARIOUS ACETONE–WATER SOLVENT MIXTURES

Vol % Acetone	U(IV) Order	U(VI) Order	H^+ Order	$k \times 10^2$
30	1.25	1.0	1.85	1.465
60	1.33	1.13	2.85* (1.0)†	2.508*
90	1.47	0.59	1.17	2.780

* H^+ conc. above 0.1 M

† H^+ conc. below 0.1 M

For the 30 vol per cent acetone–water solvent the following rate expression can be written

$$R = k_1'[UO_2OH^+][UOH^{3+}] + k_2'[UO_2^{2+}][U^{4+}] + k_3'[U_2(OH)_2^{6+}][UO_2^{2+}] \quad (21)$$

Using the following equilibrium constant

$$K_9 = \frac{[U_2(OH)_2^{6+}]}{[UOH^{3+}]^2} \quad (22)$$

and the assumptions that $[U_2(OH)_2^{6+}]$ is small and $K_2 \ll [H^+]$ as well as Equations (2) and (3), Equation (21) can be rewritten as follows

$$R = \frac{k_1[U(VI)][U(IV)]}{[H^+](K_1 + [H^+])} + \frac{k_2'[U(VI)][U(IV)][H^+]}{K_1 + [H^+]} + \frac{k_3[U(VI)][U(IV)]^2}{([H^+] + K_1)^2} \quad (23)$$

where $k_1 = k_1' K_1 K_2$ and $k_3 = k_3' K_1^2 K_9$.

Graphically, k_1, k_2' and k_3 were determined to be 3.8×10^{-3} moles l^{-1} min^{-1}, 7.0×10^{-2} l moles^{-1} min^{-1}, and 5.8×10^{-2} min^{-1}, respectively. Using these values the rates have been calculated and are tabulated in Table 6. The average deviation of R_{calc} from R_{obs} is ±8.2 per cent.

TABLE 6 — A COMPARISON OF THE OBSERVED AND CALCULATED INITIAL RATES FOR THE U(IV) U(VI) EXCHANGE REACTION IN WATER ACETONE MIXED SOLVENTS AT 25 C

[U(IV)] 10^2 (M)	[U(VI)] 10^2 (M)	[H] (M)	R_{obs} 10^5 (M min^{-1})	R_{calc} 10^5 (M min^{-1})	Deviation (%)
		30% Acetone			
2.13	1.05	0.1077	8.44	9.51	12.7
2.13	1.05	0.0912	10.83	11.42	5.4
4.27	1.05	0.0912	25.39	27.02	6.4
2.13	1.05	0.0797	13.17	14.05	6.7
3.39	0.926	0.0528	44.80	41.46	7.4
2.42	1.85	0.0574	52.85	48.12	9.0
2.42	1.30	0.0574	33.49	33.83	1.0
1.45	0.926	0.0528	16.74	14.16	15.4
4.36	0.926	0.0528	63.02	57.00	9.5
1.45	1.30	0.0528	20.21	21.11	4.4
1.45	0.370	0.0528	6.48	6.05	6.6
1.45	0.370	0.1090	1.70	1.94	14.1
					Ave 8.2
		60% Acetone (Acid 0.1M)			
1.453	0.3704	0.1099	9.86	9.87	0.1
1.453	0.3704	0.1342	6.30	5.95	5.6
1.453	0.3704	0.1136	11.37	12.24	7.7
1.453	0.3704	0.2121	1.91	2.05	7.3
1.453	0.3704	0.1434	5.46	5.04	7.7
2.977	0.5434	0.1443	17.89	27.72	
3.970	0.5814	0.1468	26.62	49.04	
0.4945	0.4484	0.1474	0.988	0.931	5.8
0.9889	0.4674	0.1488	3.06	2.98	2.6
0.9924	1.3760	0.1492	10.22	8.74	14.5
0.9924	0.8969	0.1492	5.44	5.70	4.8
					Ave 6.2
		60% Acetone (Acid 0.1M)			
1.453	0.3704	0.07859	16.36	16.67	1.9
1.453	0.3704	0.04733	11.83	12.31	4.1
1.453	0.3704	0.04037	12.04	12.00	0.3
1.453	0.3704	0.07457	14.62	16.01	9.5
1.453	0.3704	0.07457	15.15	16.01	5.7
					Ave 4.3
		90% Acetone			
0.2808	0.07191	0.1185	0.0806	0.0804	0.2
0.2808	0.07191	0.2015	0.0448	0.0445	0.7
0.2808	0.07191	0.03962	0.310	0.309	0.3
0.2808	0.2549	0.03962	0.617	0.625	1.3
0.2808	0.1938	0.03962	0.556	0.521	6.3
1.127	0.1046	0.03755	3.029	4.053	33.8
0.5636	0.0828	0.03892	0.962	1.062	10.4
					Ave 7.6

When the acetone is increased to 60 vol per cent a rather strange effect is observed. Below an acid concentration of 0.1 M the order with respect to hydrogen ion is positive, but above 0.1 M acid the order with respect to hydrogen ion is almost a negative three. This indicates a definite change of mechanism in the region of 0.1 M acid. Unfortunately, no U(IV) or U(VI) dependence data were taken in the region below 0.1 M acid. Unless otherwise stated the following discussion refers to the region above 0.1 M acid.

The following rate expression reproduced the experimental data

$$R = k_1[\mathrm{UOH}^{3+}][\mathrm{UO}_2^{2+}] + k_2[\mathrm{U}_2(\mathrm{OH})_2^{6+}][\mathrm{UO}_2\mathrm{OH}^+] \tag{24}$$

On using Equations (2), (3), and (21) and the assumptions that $[\mathrm{U}_2(\mathrm{OH})_2^{6+}]$ is small and K_2 $[\mathrm{H}^+]$, the following equation is obtained

$$R = \frac{k_1'[\mathrm{U(IV)}][\mathrm{U(VI)}]}{[\mathrm{H}^+] + K_1} + \frac{k_2'[\mathrm{U(IV)}]^2[\mathrm{U(VI)}]}{([\mathrm{H}^+] + K_1)^2[\mathrm{H}^+]} \tag{25}$$

where $k_1' = k_1K_1$ and $k_2' = k_2 K_1^2 K_2 K_9$.

Graphically, k_1' and k_2' were determined to be 2.88×10^{-2} min^{-1} and 1.86×10^{-1} moles l^{-1} min^{-1}, respectively. By using these values the rates were calculated and are tabulated in Table 6 in the first part of the 60 vol per cent acetone data. The runs with $[\mathrm{U(IV)}] > 1.5 \times 10^{-2}$ M do not fit the rate expression and it has been assumed that at high concentrations of U(IV) the mechanism changes. Excluding the runs with $[\mathrm{U(IV)}] > 1.5 \times 10^{-2}$ M, the average deviation of R_{calc} from R_{obs} is 6.2 per cent.

In the second section of the 60 vol per cent acetone data tabulated in Table VI is the comparison of R_{calc} with R_{obs} for the acid concentration range below 0.1 M. The rates were calculated from the following rate expression

$$R = k_1 [\mathrm{U(IV)}] [\mathrm{U(VI)}] [\mathrm{H}^+] + \frac{k_2 [\mathrm{U(IV)}] [\mathrm{U(VI)}]}{[\mathrm{H}^+]^2} \tag{26}$$

where k_1 and k_2 are 37 l^{2} moles^{-2} min^{-1} and 1.2×10^{-3} moles l^{-1} min^{-1}, respectively. The average deviation of R_{calc} from R_{obs} is 4.3 per cent.

The following rate expression can be written for the reaction in 90 vol per cent acetone

$$R = k_1[\mathrm{UOH}^{3+}][\mathrm{UO}_2^{2+}] + k_2[\mathrm{UOH}^{3+}][\mathrm{UO}_2\mathrm{OH}^+] + k_3[\mathrm{UOH}^{3+}]^2 \tag{27}$$

Assuming that $[\mathrm{U}_2(\mathrm{OH})_2^{6+}]$ is small, K_1 $[\mathrm{H}^+]$, and K_2 $[\mathrm{H}^+]$, and using Equations (2) and (3), equation (27) can be written as follows

$$R = \frac{k_1'[\mathrm{U(IV)}][\mathrm{U(VI)}]}{[\mathrm{H}^+]} + \frac{k_2'[\mathrm{U(IV)}] [\mathrm{U(VI)}]}{[\mathrm{H}^+]^2} + \frac{k_3'[\mathrm{U(IV)}]^2}{[\mathrm{H}^+]^2} \tag{28}$$

where $k_1' = k_1 K_1$, $k_2' = k_2 K_1 K_2$, and $k_3' = k_3 K_1^2$.

Graphically k_1', k_2' and k_3' were determined to be 4.10×10^{-2} min^{-1}, 6.41×10^{-1} mole l^{-1} min^{-1}, and 3.68×10^{-1} mole l^{-1} min^{-1}, respectively. In Table 6 are tabulated the rates calculated by use of these values for k_1', k_2' and k_3'. The average deviation of R_{calc} from R_{obs} is ±7.6 per cent.

In general, the rate laws for the acetone–water systems cannot be correlated very well with themselves or other mixed solvent data This may be partly due to the reaction between acetone and acid (9) The main difference in the acetone-water system as compared to the ethanol-water system is that in the former the specific velocity constant remains nearly constant through 90 vol per cent organic component while in the latter it increases by 1000-fold

CONCLUSION

The rate laws and therefore the mechanisms in the three organic water mixed solvent systems depend on the per cent of organic component as well as the particular organic component The dependence on per cent organic component changes radically between 90 and 98 vol per cent organic component because of the entering of the organic component into the mechanisms by solvolysis Solvation as well as dielectric probably has an effect on the rate of reaction in the various organic water mixed solvents

advantages over working with BrCl as such: it obviates the need to prepare solutions exactly equimolar in bromine and chlorine and the excess of bromine reduces the concentration of free chlorine formed by dissociation of BrCl to a very low value.

Bromine solutions were prepared by making stoichiometric mixtures of potassium bromate and HBr in 2N perchloric acid solution. The chlorine was taken from part-emptied cylinders (ex I.C.I.).

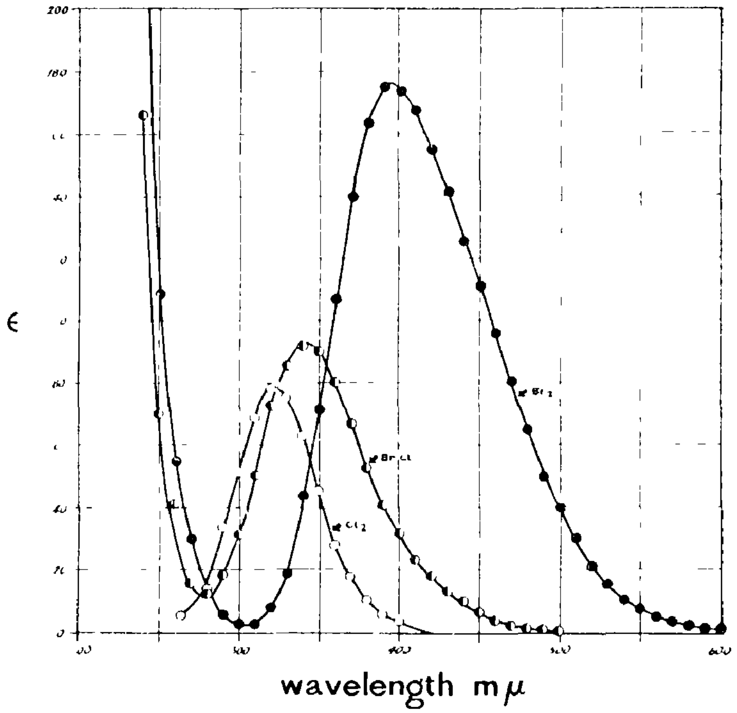


FIG. 1. Extinction coefficients versus wavelength (mμ). Measured in 2N perchloric acid solution.
● Br_2 ◖ BrCl, ○ Cl_2

The total halogen concentration was measured iodometrically using N/50 thiosulphate. Absorption measurements were made on a Unicam S.P. 500 Spectrophotometer. 10 cm cells were used for wavelengths greater than 450 mμ and 1 cm cells below 450 mμ. At wavelengths greater than 500 mμ absorption was found to be due entirely to bromine and the concentration of bromine in each solution was calculated from measurements made between 550 and 500 mμ using 10 cm cells. At shorter wavelengths the total absorption (a) is given by

$$a = \epsilon_{BrCl}[BrCl]d + \epsilon_{Br_2}[Br_2]d \qquad (1)$$

where ϵ_{BrCl} and ϵ_{Br_2} are the extinction coefficients of BrCl and Br_2 and d is the length of the absorption cell. If the total halogen concentration is C, then

$$[BrCl] = C - [Br_2]$$

whence the absorptivity,

$$A = \frac{a}{Cd} = \epsilon_{BrCl} + \frac{[Br_2]}{C}(\epsilon_{Br_2} - \epsilon_{BrCl}) \qquad (2)$$

For each wavelength the plot of absorptivity against $[Br_2]/C$ is a straight line, the intercept being equal to ϵ_{BrCl}. The extinction coefficients for BrCl so obtained are shown in Fig. 1. The extinction curve has a peak at the wavelength reported by Pungor, Burger and Schulek as giving maximum absorption (343 mμ).

Fig. 1 also shows the extinction curves for aqueous Br_2 and Cl_2. The latter was obtained from measurements made on solutions of chlorine and chloride ions in 2N perchloric acid; the extinction

---

G. ZIMMERMAN and F. C. STRONG, *J. Amer. Chem. Soc.* **79**, 2063 (1957).

J. Inorg. Nucl. Chem. 1963. Vol. 25, pp. 1457 to 1463. Pergamon Press Ltd. Printed in Northern Ireland

ANION EXCHANGE OF METAL COMPLEXES—XIII

THE ACTINIDE(III)–NITRATE SYSTEM(1)

Y. MARCUS and M. GIVON
Radiochemistry Department
Israel Atomic Energy Commission,
Soreq Research Establishment,
Rehovot, Israel

and

G. R. CHOPPIN
Department of Chemistry, Florida State University
Talahassee, Fla., U.S.A.

(*Received* 24 *January* 1963)

Abstract—Anion exchange distribution data were obtained for a number of trivalent actinide ions (Pu, Am, Cm, Bk, Cf and Es) in lithium nitrate solutions. The distribution coefficients are comparable with those of the lanthanide group, so that no group separation is possible, but within the actinide group an efficient separation of americium and curium was found. Extraction behaviour by long chain amines followed that of the lanthanides, but in reverse atomic number order. A second power dependence of distribution coefficients on amine concentration was found.

A STUDY of the anion exchange behaviour of the trivalent actinides in nitrate is interesting, particularly in the light of the anomalous behaviour shown by the corresponding lanthanides.(2) A general trend of decreasing distribution coefficients, D, with increasing atomic numbers Z has been found for the latter series, which corresponds to D increasing with the crystalline radius (r). This trend is reversed, however, on going from lanthanum (r = 1.06 Å) to actinium (r = 1.11 Å), as pointed out by DANON(3), who predicted the absorbability order Ac > Pu(III) > Am, based on the meager data then available. A further anomaly, the odd-even effect found for the lanthanides,(2) should be even more important in the actinide series, if it is due, as presumed, to ligand-field effects, which should be more important with $5f$ than with $4f$ electrons. The extraction of the trivalent actinides by tri-n-butyl phosphate(4) does show a lower extractability for curium $5f$ than expected from the smoothly changing ionic radii. An odd-even Z effect, although not similar in detail, has also been found in the anion exchange distribution coefficients of lanthanides and actinides in concentrated lithium chloride(5) and ammonium thiocyanate.(6)

Previous reports on the anion exchange of the trivalent actinides mainly stressed that unlike the higher oxidation states, they are not absorbed from nitric acid,(7) although absorption from concentrated lithium nitrate solutions has been demonstrated.[2,8,10] Quite similarly, the distribution coefficients of plutonium (III) and americium between dilute solutions of a long chain amine and nitric acid have been found to be negligible[11] whereas extraction from low acid high nitrate solutions was appreciable.[12] It may thus be anticipated that significant results would be obtained for the distribution coefficients of the trivalent actinides in both anion exchange and amine extraction from lithium nitrate solutions.

---

(1) Based on Israel Atomic Energy Commission Report IA-783, October 1962, by Y. MARCUS and M. GIVON, and communications from G. R. CHOPPIN.

(2) Y. MARCUS and F. ABRAHAMER, *J. Inorg. Nucl. Chem.* **22**, 141 (1961).

(3) I. DANON, *J. Inorg. Nucl. Chem.* **7**, 422 (1958).

(4) G. F. BEST, E. HESFORD, and H. A. C. MCKAY, *J. Inorg. Nucl. Chem.* **12**, 136 (1959).

(5) E. K. HULET, R. G. GUTMACHER and M. S. COOPS, *J. Inorg. Nucl. Chem.* **17**, 350 (1961).

(6) J. P. SURLS, JR. and G. R. CHOPPIN, *J. Inorg. Nucl. Chem.* **4**, 62 (1957).

(7) R. F. BUCHANAN and J. P. FARIS, *Conference on Use of Radioisotopes in Physics, Science and Industry*, 7 Copenhagen, paper RICC/173 (1960).

EXPERIMENTAL

^{239}Pu and ^{241}Am were obtained from O.R.N.L., and ^{244}Cm, ^{249}Bk, ^{252}*Cf and ^{253}Es were kindly supplied by Drs. B. B. Cunningham, S. Fried and J. C. Wahlman, Lawrence Radiation Laboratory, Berkeley. Lithium nitrate solutions were kept slightly acid (about 5 mM HNO_3) to avoid hydrolysis. The amines used were tri-iso-octylamine (TIOA) diluted with xylene, and Alamine 336, a C_8–C_{10} tertiary amine diluted with toluene. The resin was Dowex 1X10 in nitrate form, 100–200 mesh for the columns, 50–100 mesh for the batch experiments, but different batches of resin were used in Florida, in Berkeley and in Israel.

Anion exchange data were obtained by column elutions at 87°, as previously described,[8] except for some data on americium and all data for plutonium (III), which were obtained by batch equilibration at room temperature. Relative concentrations in lithium nitrate solutions were obtained for Pu, Am, Cm, Cf and Es by α-counting after dilution, extraction with 30 per cent Alamine 336 in toluene or co-precipitation with a small amount of LaF_3, to avoid self-absorption by deposits on the counting plates. ^{252}Cf was also determined by spontaneous fission counting, while a windowless proportional counter was used for the soft betas of ^{249}Bk. Plutonium was equilibrated inside spectrophotometer cells,[13] and was kept at the +3 oxidation state by 15 mM hydrazinium nitrate both in the aqueous phase and in the resin, as found by sequential partial desorption when the aqueous phase was diluted stepwise. The spectrophotometric results agreed well with α-counting data. The loading of the resin with plutonium was kept below 1 per cent.

The amine extraction equilibrations were made at room temperature by shaking pre-equilibrated diluted and neutralized amine with aqueous lithium nitrate solutions. Distribution coefficients were calculated from the decrease in the α-activity in the organic phase, the tracer being initially in this phase.

RESULTS

Anion exchange volume distribution coefficients for Pu(III), Am, Cm, measured in Israel, Cm, Cf, and Es measured in Berkeley, and Am, Cm and Bk measured in Florida are shown in Fig. 1 as function of lithium nitrate molality. Weight distribution coefficients obtained for plutonium (III) and americium were divided by 2.2 ml/g, the specific volume of the resin, to obtain volume distribution coefficients (variation of the specific volume with salt molality were neglected). The values for Cm obtained with the various batches of resin by workers in various laboratories are seen to agree well. Those for Am, obtained by Choppin in Florida, are however lower than those obtained by Marcus and Givon in Berkeley and Israel. The disagreement between the two sets of data is not fully understood, but cannot be ascribed

---

* The sample contained some ^{254}Cf and ^{253}Cf, which caused a slow growing-in of ^{253}Es.

(8) Y. Marcus and F. Nelson, *J. Phys. Chem.* **63**, 77 (1959).

(9) H. H. Lloyd, and R. H. Leuze, U.S.A.E.C. Report CF-60-3-23 (1960).

(10) S. Adar, R. K. Sjoblom, R. F. Barnes, P. R. Fields, E. K. Hulet and H. D. Wilson, *J. Inorg. Nucl. Chem.* **25**, 447 (1963). S. Adar, Private communication.

(11) W. E. Keder, J. C. Sheppard and A. S. Wilson, *J. Inorg. Nucl. Chem.* **12**, 327 (1962).

(12) C. F. Coleman, U.S.A.E.C. Report TID-7607 (1961).

(13) Y. Marcus, Israel AEC Report R 20 (1959).

to error since the separation factors were reproducible in both cases It might be due to high sensitivity to acidity,[8] and slight differences in equilibrium concentration of nitric acid in the two sets of data In fact, the results of Am obtained by CHOPPIN agree with those obtained by ADAR *et al*[10] at 5 mM HNO_3 (batch experiments) or 10 mM HNO_3 (elutions), whereas those of MARCUS and GIVON were obtained at 1 2 mM HNO_3 (batch experiments and elutions) The distribution of Cm seems

to be less sensitive to acid concentration The considerable gap between the curves for americium and curium suggests efficient separations between these two neighbouring actinides, two examples being shown in Fig 2

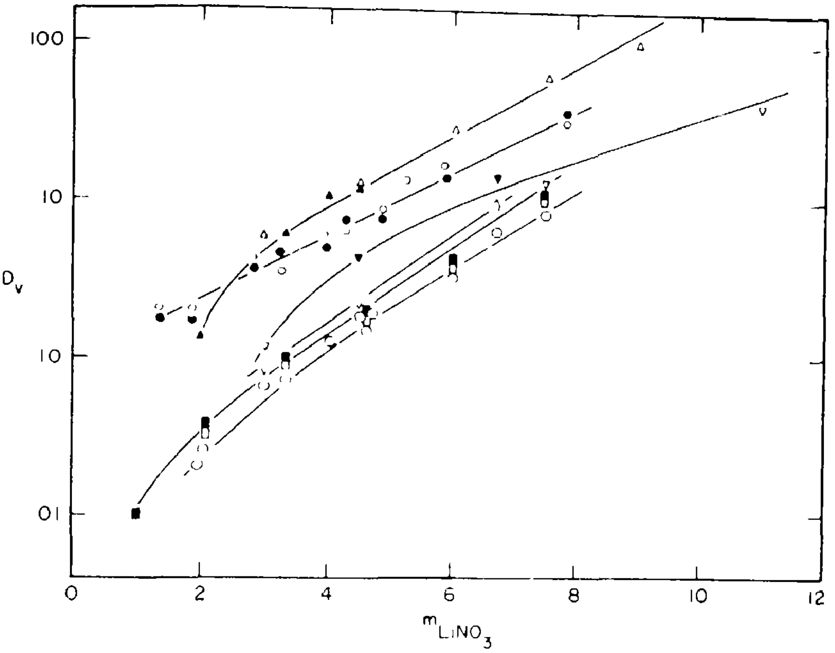


FIG 1 Volume distribution coefficients for trivalent actinides on Dowex-1 vs lithium nitrate molality ● Pu batch experiments spectrophotometry, Pu same experiments radiometric determinations Am calculated from batch experiments[2] Am from ref (9) ▲ Am, column elutions 2 mM HNO_3 (data from Israel) ▼ Am column elutions, probably 5-10 mM HNO_3[10] (data from Florida) Bk Cf ■ Es

Distribution coefficients of Am Cm Cf and Es between solutions of tertiary amines in aromatic diluents and 7 5 m $LiNO_3$ are shown in Fig 3 Data for Pu(III) could not be obtained even in the presence of iron(II) sulphamate hydrazinium nitrate and other reducing agents which though sufficient to keep the plutonium in the +3 oxidation state in lithium nitrate solutions could not prevent the oxidation in the amine phase, as shown by spectrophotometric evidence[11] Data were obtained also for other lithium nitrate concentrations and the distribution coefficients were found to increase with increasing concentration as for the anion exchange resin (Fig 1)

---

[11] M GIVON, Y MARCUS and I ABRAHAMER (To be published)

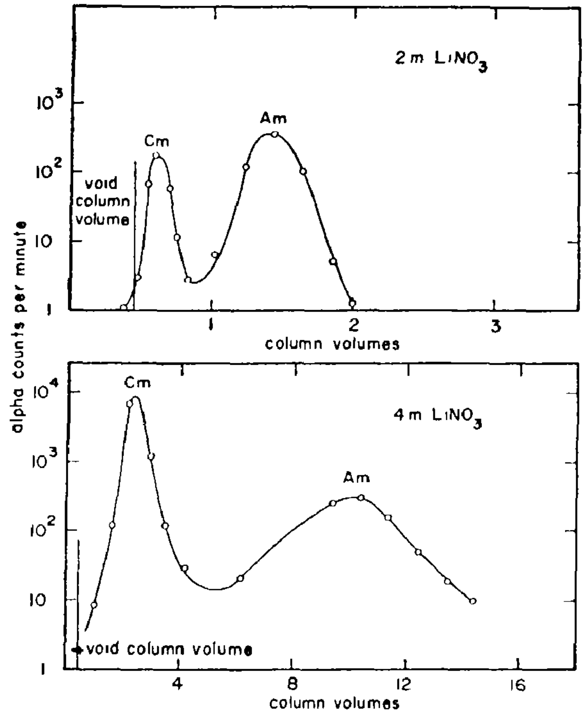


FIG. 2.—Separation of americium and curium on a Dowex 1X10, 100–200 mesh column, 0.032 cm^2 cross-section, 7.5 cm long. Eluant flow-rate 1.2 cm/min, temperature 87°C, acidity 2 mM HNO$_3$.

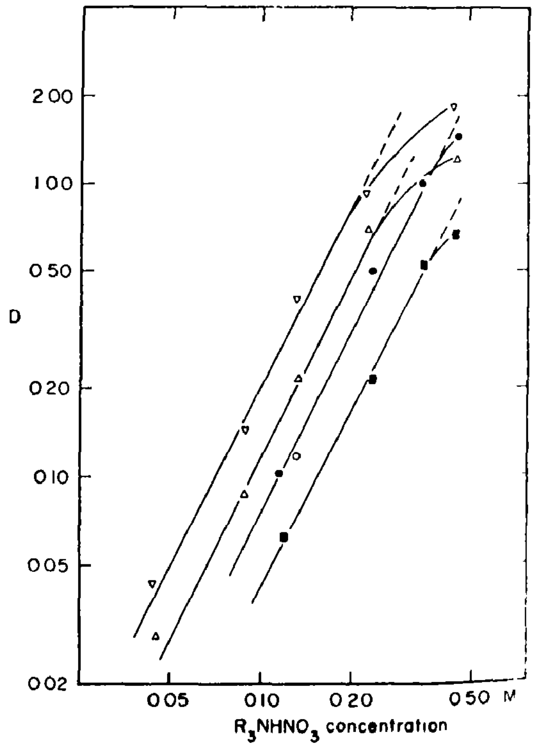


FIG. 3.—Distribution coefficients of Es ▽, Cf △, Cm , and Am □, between Alamine 336 nitrate in toluene (open symbols) or tri-iso-octyl-ammonium nitrate in xylene (full symbols) and 7.5 m lithium nitrate solutions, as function of amine concentration.

DISCUSSION

An obvious conclusion from the data is that the actinides behave, on the whole, very similarly to the lanthanides. Thus the slope of the log-log plots in Fig. 3 is +2.00, as found for cerium, europium and lutecium,(2) signifying a species $R_2M(NO_3)_5$ in the organic phase [R = $(C_8H_{17})_3NH^+$, M^{3+} = actinide cation). The order of increasing distribution coefficients for the three lanthanides follows the order of *Z* whereas the reverse occurs with the actinides, the order for amine extraction being Es > Cf > Cm > Am. For the anion exchange distribution, the distribution coefficients for lanthanides(2) and actinides are plotted vs. *Z* for 5 m $LiNO_3$ in Fig. 4.

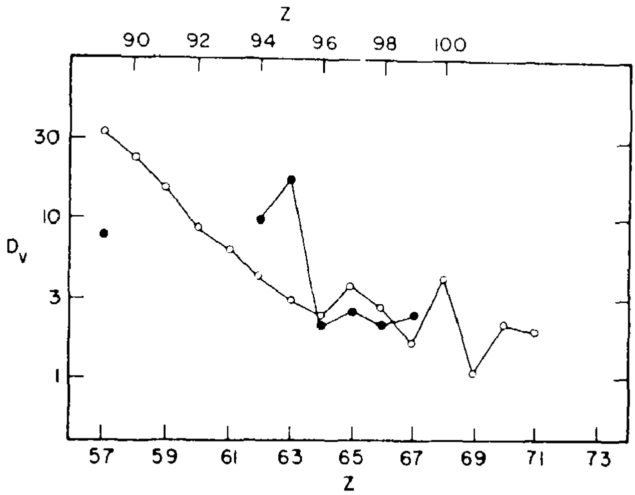


FIG. 4.—Volume distribution coefficients for trivalent actinides and lanthanides on Dowex 1 for 5 m lithium nitrate vs. the atomic number. ○ lanthanides (lower abscissa) ● actinides (upper abscissa).

The value for actinium was taken from DANON's work.(3) The order of the elements Am > Pu > Ac follows that which was predicted by DANON.( ) The character of trend in D_v from Pu to Es is quite different from that from Sm to Ho. Considering the uncertainity in the relative D_v values for the elements Cm, Bk, Cf and Es—individual D_v values having errors of ±10 per cent—no even-odd effect can be seen for this set of four elements. However, the slowly increasing trend from Cm to Es (separation factor approximately 1.4) is opposed to the trend with the preceding elements Pu and Am. The features of the overall trend for the D_v values from anion exchange for Pu to Es are different from those observed with TBP extraction from nitric acid,(1) and are rather the opposite from those observed with anion exchange from lithium chloride(5) and ammonium thiocyanate(6) solutions.

If one considers only the ions $Y^{3+}(3f^{0})$, $La^{3+}(4f^{0})$, $Gd^{3+}(4f^{7})$, $Lu^{3+}(4f^{14})$, $Ac^{3+}(5f^{0})$ and $Cm^{3+}(5f^{7})$, there should be no interference of ligand field effects, which may cause the odd-even *Z* effect. The distribution coefficients should then be a smooth function of the ionic radius, which alone should determine the electrostatic interaction. Indeed, for 9 m $LiNO_3$ a plot of log *D* vs. *r*, produces a smooth curve except for actinium, which behaves like an ion with a radius 0.09 Å smaller (Fig. 5). On going to lower concentrations, however, where invasion of the resin is smaller, and the two

phases are less alike. The data seem to split into different components for the fifth, sixth and seventh period elements (Fig. 5)

It is also difficult to correlate the anion exchange results with known nitrate complexing in solution. For the lanthanides the anion exchange log D vs Z pattern reproduces the log k_1 vs Z pattern obtained from cation exchange,(16) where k_1 is the equilibrium quotient for the reaction $M^{3+} + NO_3^- \rightleftharpoons MNO_3^{2+}$. For the actinides, the complexing data are more restricting, the values log k_1 = 0.77 for Pu(III),(17) log k_1 = 0.60 for Am(18) and log k_1 = 0.57 for Cm(18) having been published. The order here does not agree with the anion exchange absorbabilities (Fig. 4).

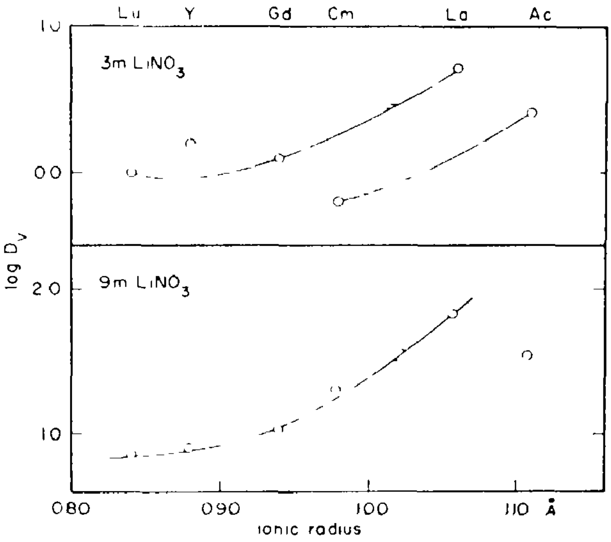


FIG. 5.—Volume distribution coefficients for trivalent Y($3f^0$), La($4f^0$), Gd($4f^7$), Lu($4f^{14}$) Ac($5f^0$) and Cm($5f^7$), as function of crystalline radius,(15) for 3 and 9 m lithium nitrate. The dashed circles are the values for Ac for 0.09 Å smaller radius.

However, these values for k_1, precise to within ±10 to ±20 per cent, need not bear a direct relation to the anion exchange distribution, which probably involves anionic complexes. Trends in association constants are known to vary when complexing proceeds with more and more ligands.

The results of studies on anion exhange of lanthanides and actinides in concentrated lithium nitrate(2,8) or chloride(5) have unfortunately raised more questions than they have solved. Study of α-emitting nuclides in concentrated salt solutions are rather difficult experimentally so that precise absolute, or even relative values of the distribution coefficients are hard to obtain. Since the addition our knowledge of the physical chemistry of concentrated salt solutions and ion exchange resins in equilibrium with these solutions is so incomplete, more than a qualitive interpretation of the results cannot be ventured. Ligand-field effects may be the cause of the baffling even-odd Z effect, and the difference between the actinides and the lanthanides.

---

(15) W. H. ZACHARIASEN, *The Actinide Elements* (Edited by G. T. SEABORG, and J. J. KATZ) Chap. 18, McGraw-Hill, New York (1954).

(16) J. DANON, Private communication (1962).

(17) V. B. SHEVCHENKO, V. G. TIMOSHEV and A. A. VOLKOVA, *Atomnaya Energiya* **6**, 427 (1959).

(18) I. A. LEBEDEV, S. V. PIROZHKOV and G. N. YAKOVLEV, *Akad. Nauk* S.S.S.R. Ordena Lenina Inst. Atom. Energ. 1960 (English translation U.S.A.E.C. Report AEC-tr-4275).

Acknowledgements—We would like to thank L. COHEN and H. ACKERMAN (Israel Atomic Energy Commission) and E. MEYER and W. CAMPBELL (Florida State University) for their technical aid in obtaining the data for the above work. We would like also to express our appreciation to Profs. B. B. CUNNINGHAM and I. PERLMAN, Lawrence Radiation Laboratory, University of California, Berkeley, for enabling Y. MARCUS to carry out part of this work during his stay at the Lawrence Radiation Laboratory, in Summer of 1961.

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 1465 to 1470. Pergamon Press Ltd. Printed in Northern Ireland

THE ANION EXCHANGE OF METAL COMPLEXES—XI*

APPLICATION OF THE CONSTANT IONIC MEDIUM METHOD TO THE MERCURY HALIDE SYSTEM

I. Eliezer and Y. Marcus
Radiochemistry Department, Israel Atomic Energy Commission,
Soreq Research Establishment, Rehovoth, Israel

(*Received* 26 *March* 1963; *in revised form* 10 *May* 1963)

Abstract—The applicability of the constant ionic medium method to the study of metal complex formation by exchange has been investigated, using the mercury(II) halide system as an illustration. The distribution of mercury(II) tracer has been measured between C molar (NaX + $NaClO_4$) solution and (RX + $RClO_4$) Dowex 1 resin, for C = 0.3, 0.5 and 3.0 M and X = Cl^-, Br^- and I^-. The stability constants for the resin phase and for the 0.3 and 3 M solutions have been calculated. The general applicability of the method for anion exchange studies has been discussed.

THE constant ionic medium method[(1)] has often been used to study complex formation in solution. It has been used successfully in conjunction with the cation exchange method[(1b)] but less successfully with the anion exchange method. FRONAEUS,[(2)] in introducing anion exchange as a quantitative method for studying metal complexes, mentioned that if a constant neutral salt medium is used, considerable anion exchange takes place when the ligand concentration is varied within wide limits, and the metal distribution will be a too complicated function of the ligand concentration. Subsequent quantitative treatments of the anion exchange method[(3,4)] have usually dispensed with a constant ionic medium, and tried instead to evaluate the activity coefficient terms.

A detailed examination of the applicability limits of the constant ionic medium method seemed desirable, because of the known difficulties with the evaluation of activity coefficients. While this work was in progress, FRONAEUS *et al.*[(5)] published an account of the use of this method obtaining the stability constants in the resin phase for the cadmium bromide system, without however evaluating it in a general way. Earlier, SONESSON[(6)] studied the gadolinium glycolate system using a constant ionic medium in the aqueous phase, while permitting the resin composition to vary considerably. The medium inside the resin was, therefore, far from constant, and stability constants in the resin phase could be determined very approximately, using constants for the aqueous phase obtained by another method Similarly, in the method proposed by Waki,[7 9] substitution was permitted to proceed over the whole mole fraction range, and it is unlikely that the activity coefficient term remained constant The differentiation used may therefore not be reliable Further complications are introduced in Waki's experiments by the considerable loading of the exchanger by the metal used

---

* Previous paper in Series: D. MAYDAN and Y. MARCUS, *J. Phys. Chem.* **67**, 987 (1963).

(1) J. N. BRONSTED, *Trans. Faraday Soc.* **23**, 416 (1927).

(1b) F. J. C. ROSSOTTI and H. ROSSOTTI, *Determination of Stability Constants*. McGraw-Hill, New York (1961).

(2) S. FRONAEUS, *Svensk Kem. Tidskr.* **65**, 1 (1953).

(3) Y. MARCUS and C. D. CORYELL, *Bull. Res. Council* **8** A, 1 (1959).

(4) K. A. KRAUS and F. NELSON, *Structure of Electrolyte Solutions* (Edited by W. J. HAMER), p. 340. J. Wiley, New York (1959).

(5) S. FRONAEUS, I. LUNDQVIST and A. SONESSON, *Acta Chem. Scand.* **16**, 1936 (1962).

(6) A. SONESSON, *Acta Chem. Scand.* **15**, 1 (1961).

It does not seem possible, in a completely general way, to vary the ligand concentration over a wide range and still have a constant ionic medium in the resin phase In some particular cases, however, this may be possible Namely, this is so where complex formation is relatively strong, requiring only low concentrations of the ligand, and where the affinity of the ligand for the resin is not too high, so that the resin remains essentially loaded with the medium ions Using perchlorate ions for the medium, as is usually done, has the advantage of providing the resin with an anion of high affinity, competing favourably with most ligand ions This requires high intrinsic affinity of the anionic metal complex for the exchanger, as otherwise distribution coefficients would be too small In cases fulfilling the above requirements, it should be possible to determine stability constants for both phases, valid for the ionic medium chosen, and particularly also constants for the anionic complexes, which may not be always reliably determined by other methods For other cases, in particular where complexes are weak and are formed only at high ligand concentration, the constant medium principle cannot be used, and other anion exchange methods[1] should be used

The present work describes the application of the constant ionic medium method to the mercury halide systems, where the above conditions seem to have been met The stability constants for mercury(II) with chloride, bromide and iodide have already been measured by other methods [10 12]

The values obtained by the anion exchange method may thus be compared with previously reported values

EXPERIMENTAL

Materials Radioactive mercury, ^{203}Hg, obtained from O R N L in form of a nitrate solution was used, diluted so that the total mercury concentration was in all cases 10^{-4}-10^{-6} M The resin used was *Bio-Rad Dowex-1 A G*, 8 per cent crosslinked, 100 200 mesh It was converted to the appropriate halide form, using hydrochloric acid, sodium bromide or iodide, after having been passed through the usual acid base conditioning cycles All other reagents were of analytical grade

Methods Selectivity coefficients, $K^{X}_{ClO_4}$ $(\overline{X^-})(ClO_4^-)/(\overline{ClO_4^-})(X^-)$, parenthesis denoting concentrations, barred symbols the resin phase, and X a halide ion, were measured in experiments where known quantities of resin in halide form were equilibrated for 24 hours with known quantities of perchlorate solutions at room temperature, 23 ± 3° The coefficients were calculated from the measured capacity of the resin, its water content (obtained by the centrifugation method)[13] and the concentration of halide in the resin and the solution phases at equilibrium

Mercury distribution coefficients were measured in similar experiments Weighed amounts of

---

[7] H Waki, *Bull Chem Soc Japan* **33,** 1469 (1960), **34,** 829 (1961)

[8] H Waki, *Bull Chem Soc Japan* **34,** 1842 (1962)

[9] J Yoshimura, H Waki and S Tashiro, *Bull Chem Soc Japan* **35,** 412 (1962)

[10] L G Sillen, *Acta Chem Scand* **3,** 539 (1949)

[11] Y Marcus, *Acta Chem Scand* **11,** 599 (1957)

[12] C L Van Pantaleon Van Eck, Thesis, Leiden (1958).

[13] K W Pepper, D Reichenberg and D K Hale, *J Chem Soc* 3129 (1952)

coefficients being derived by the method of ZIMMERMAN and STRONG.(3) The bromine extinction coefficients were obtained from the slopes of the lines corresponding to equation (2) and showed reasonable agreement with values obtained by the application of the ZIMMERMAN and STRONG technique to solutions containing bromine and bromide ions.

Research & Development Department
The Associated Octel Company Limited
Ellesmere Port
Cheshire

J. R. GROVE
L. RAPHAEL

The infra-red spectrum and structure of I_2O_4

(*Received* 13 *June* 1962)

WISE and HANNAN(1) in a recent paper claim to have shown that iodine dioxide consists of discrete IO^+ and IO_4^- ions. Since their work is at variance with our earlier and more extensive investigations(2,3) we propose to discuss why we believe WISE and HANNAN's assignments are wrong and briefly to recapitulate the results of our own work.

We feel that the reasons for the difference between WISE and HANNAN's results and our own lie (a) in their failure to measure spectra at wave numbers below 650 cm^{-1} and (b) in their use of KBr discs instead of Nujol mulls. Their failure to measure peaks below 650 cm^{-1} meant that they failed to observe a group of peaks in the 550–650 cm^{-1} region which cannot be attributed to an unco-ordinated iodate ion. We made up a KBr disc of I_2O_4 to compare its spectra with our own run in Nujol and observed the following points:

(1) their "IO" band at 9.05 μ (1105 cm^{-1}) occurred in a blank KBr disc and, we suspect, may be due to moisture.

(2) the quality of the I_2O_4 spectrum obtained depended on the length of time the KBr and the I_2O_4 were ground together before pressing into a disc. Extended milling reduced the intensity of the peaks between 550–650 cm^{-1} and the disc became a deep brown in colour. We feel that this is due to reaction of the I_2O_4 with the KBr to produce KIO_3 and other species

$$I_2O_4 + KBr \rightarrow KIO_3 + IBrO$$

IBrO like Br_2O presumably decomposes to IBr and O_2. Other research workers have stressed the danger of exchange taking place when using KBr discs to study the infra-red spectra of inorganic compounds.

In our paper(3) we reported an investigation of the infra-red spectra of iodine dioxide, iodosyl sulphate, $(IO)_2SO_4$ and the new iodosyl selenate $(IO)_2SeO_4$ as well as that of an organic iodo-compound known to contain I-O-I bridges, μ-oxo-dinitratodiphenyldiiodine $\phi I(NO_3)O(NO_3)I\phi$. None of these compounds contained a band at 9.05 μ (1105 cm^{-1}). Apart from the sulphate and selenate bands the two iodosyl compounds showed bands at respectively 562 and 577 cm^{-1} and 553 and 600 cm^{-1}. The I-O-I stretch in the μ-oxodinitratodiphenyldiiodine was identified as occurring at 585 cm^{-1}. The spectrum of iodine dioxide was more complicated and is reproduced below, together with those of $K_2Mn(IO_3)_6$, KIO_3 and $(IO)_2SO_4$; there is no evidence of a band at 9.05 μ.

The I_2O_4 spectrum can be explained fully in terms of polymerized I-O-I chains and IO_4 group, in which the IO_4 groups are linked to the chains by bonds comparable in co-valent character with the iodate-metal bonds in iodato complexes.

Quite apart from the infra-red spectral evidence in favour of polymerized I-O-I groups in the compounds mentioned above we considered it unlikely that these compounds contained the simple iodosyl, IO^+, cation on the following grounds:

(1) Apart from the small solubility of the sulphate and the selenate in the concentrated parent acid, none of the iodosyl compounds show any sign of solubility (without decomposition) in any of a wide range of solvents tested, including those, like nitromethane, which dissolve nitrosonium salts. This insolubility is surprising if the compounds are indeed salts containing a univalent cation, and strongly suggests a polymerized structure.

(2) By analogy with the O_2, SO, SeO, and TeO molecules, which contain the same number of valency electrons, the IO^+ ion might be expected to have a $^3\Sigma^-$ ground state and hence be paramagnetic. Iodosyl sulphate, iodosyl selenate and iodine dioxide are all diamagnetic.

(1) J. H. WISE and H. H. HANNAN, *J. Inorg. Nucl. Chem.*, **23**, 31 (1961).
(2) W. E. DASENT and T. C. WADDINGTON, *J. Chem. Soc.* (*Lond.*), 2429 (1960).
(3) W. E. DASENT and T. C. WADDINGTON, *J. Chem. Soc.* (*Lond.*), 3350 (1960).

resin in halide form were equilibrated with solutions containing 0.01 M perchloric acid (to prevent hydrolysis of mercury ions) and 0.29, 0.49 or 2.99 M sodium perchlorate. The radioactivity of aliquots of the solution, separated from the resin by filtering through glass wool plugs, was measured in a well-type scintillation counter, and compared with that of blanks, shaken under similar conditions but without resin. The distribution coefficients D (activity per gramme air dried resin/activity per ml solution) were calculated from these values.[14]

The concentrations of halide ions in solutions were determined by titration with silver nitrate, using the Mohr method for chloride and bromide, and eosin indicator for iodide. Halide concentrations in the resin were determined after displacement with excess sodium perchlorate. The results checked with those calculated from material balance within 3 per cent.

RESULTS AND CALCULATIONS

Selectivity coefficients. The values obtained for $K^{Cl}_{ClO_4}$ were $(3.3 \pm 0.4) \times 10^{-2}$ for 0.5 M and $(3.1 \pm 0.5) \times 10^{-2}$ for 0.3 M total concentration, the fraction of resin in Cl-form being in the range 0.01–0.1. No value could be obtained for the 3 M series, because of the immeasurably small concentration of chloride remaining in the resin. Although preliminary experiments indicated the possibility of a dependence of selectivity coefficients on the ionic strength of the solutions,[15] no convincing proof of this was obtained, and for similar systems,[16] no such dependence was found, the range investigated being 0.001–0.1 M only, however. The value $K^{Cl}_{ClO_4} = 0.033$ was, therefore, used for all calculations. For bromide and iodide the values $(10 \pm 1) \times 10^{-2}$ and $(33 \pm 5) \times 10^{-2}$ respectively were found for $K^{X}_{ClO_4}$ for 0.5 M total concentration. These agree fairly well with values in the literature[17] for 0.1 M solutions and were therefore, used for all the concentrations studied. From the selectivity coefficients, values of $\bar{X} = f(X)_C$ could be calculated (writing $\bar{X} = (\overline{X^-})$, the halide concentration in the resin, in moles per kilogram air dried resin, and $X = (X^-)$ in moles per litre solution)

$$\bar{X} = K^{X}_{ClO_4}\bar{C}X/[C - X(1 - K^{X}_{ClO_4})] \qquad (1)$$

where C is the total concentration in solution (0.30, 0.50 and 3.00 M), and $\bar{C}$ is the capacity of the resin in millequivalent/gramme air dried resin.

Mercury distribution. The results for the nine series of measurements are shown in Fig. 1. The amounts of resin and solution were chosen in such a way as to obtain maximal equilibrium halide concentrations of 0.10, 0.15 and 0.25 M for the three total concentrations 0.30, 0.50 and 3.00 M respectively, for each halide.

As the measurements were made under conditions of a large excess of halide over mercury, the only species present in appreciable amounts in both resin and solution phases are HgX_2, HgX_3^- and HgX_4^{2-}.[10] The following equilibria exist

$$HgX_2 + X^- \rightleftharpoons HgX_3^-, \text{ equilibrium constant } K_3 \qquad (2)$$

$$HgX_2 + 2X^- \rightleftharpoons HgX_4^{2-}, \text{ equilibrium constant } K_{34} \qquad (3)$$

$$\overline{HgX_2} \rightleftharpoons HgX_2, \text{ equilibrium constant } K_0 \qquad (4)$$

and reactions corresponding to (2) and (3) in the resin phase, with equilibrium constants $\bar{K}_3$ and $\bar{K}_{34}$ respectively The distribution coefficient will then be given by

---

[14] I. Eliezer and Y. Marcus, Israel A.E.C. Semi-annual Report July-Dec. 1961. IA 726, p. 58 (1962).

[15] I. Eliezer and Y. Marcus, Israel A.E.C. Semi-annual Report July-Dec. 1960 IA-620, p. 37 (1961).

[16] H. P. Gregor, J. E. Belle and R. A. Marcus, *J. Amer. Chem. Soc.* **77**, 2713 (1955).

[17] R. M. Wheaton and W. C. Bauman, *Industr. Engng. Chem.* **43**, 1088 (1951).

$$D = \frac{\sum_{2(\overline{\mathrm{HgX}_n})}^{4}}{\sum_{2(\mathrm{HgX}_n)}^{4}} = K_0 \frac{1 + \bar{K}_3\bar{X} + \bar{K}_{34}\bar{X}^2}{1 + K_3X + K_{34}X^2} \tag{5}$$

This relation is not sufficiently sensitive to permit the calculation of all five constants directly from it Moreover, accurate values of K_3 and K_{34} in 0 5 $NaClO_4$ solution have been obtained previously,⁽¹¹⁾ and it is of little interest to redetermine them Rather, these values can be combined with the data for the 0 5 M series, in order to reduce the number of the constants to be determined to three the stability constants

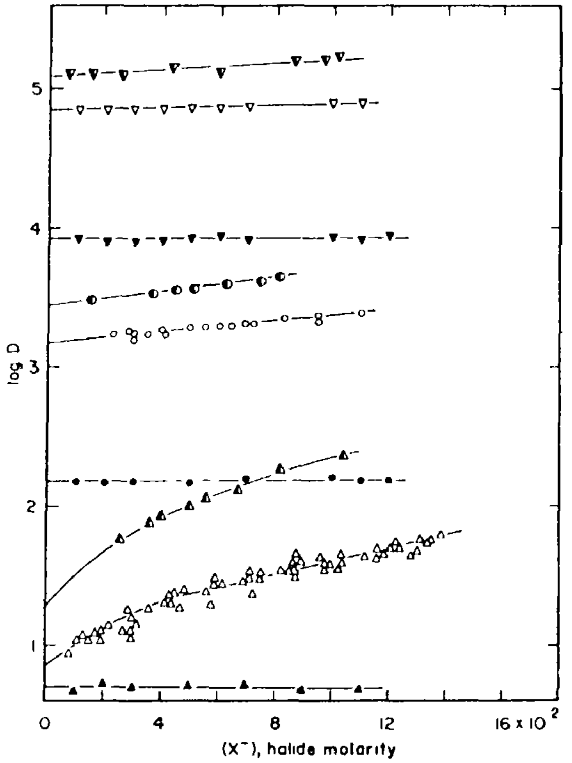


FIG 1 —Distribution coefficients for tracer mercury (II) between Dowex-1 anion exchanger and halide-perchlorate solutions △ chloride, ○ bromide, ▽ iodide, full symbol C = 3 0 M, empty symbol C 0 5 M, half-full symbol C = 0 3 M

in the resin and the distribution constant of the neutral complex between the two phases

Making use of the reported⁽¹¹⁾ K_3 and K_{34}, the denominator on the right hand side of Equation (5) was calculated and the function $t = f(\bar{X})_{0\ 5}$ (for ($C = 0\ 5$ M) was obtained

$$t = [D(1 + K_3X + K_{34}X^2) - K_0]/K_0 = \bar{K}_3\bar{X} + \bar{K}_{34}\bar{X}^2 \tag{6}$$

The constant K_0 was obtained simply by extrapolating the data to $X = 0$ Values of $\bar{K}_3$ and $\bar{K}_{34}$ were then obtained using the following methods A plot of $t\bar{X}^{-1}$ vs $\bar{X}$ gave $\bar{K}_3$ as intercept and $\bar{K}_{34}$ as slope, while a plot of $t\bar{X}^{-2}$ vs $\bar{X}^{-1}$ gave $\bar{K}_3$ as slope and $\bar{K}_{34}$ as intercept The constants could be obtained also by least squares calculation these linear functions. Alternatively, curve fitting(18) was applied, comparing the experimental curve log t vs log $\bar{X}$ with a calculated curve log ($v + v^2$) vs log v, obtaining the constants from the position of the origin of coordinates when the curves coincide.

TABLE 1

Ligand	Constant	Medium 0.3 M	0.5 M	3.0 M	resin (~12M) a	b
Chloride	log K_0 (ml g^{-1})	1.34 ± 0.08	0.90 ± 0.07	0.70 ± 0.07		
	log K_3 (M^{-1})	1.1 ± 0.1	0.95^c	0.70 ± 0.07	2.15 ± 0.07	1.55
	log K_{34} (M^{-2})	2.3 ± 0.1	2.00^c	1.30 ± 0.07	4.30 ± 0.08	3.10
Bromide	log K_0 (ml g^{-1})	3.45 ± 0.07	3.15 ± 0.09	2.18 ± 0.09		
	log K_3 (M^{-1})	2.5 ± 0.1	2.27^c	1.6 ± 0.1	2.7 ± 0.1	2.1
	log K_{34} (M^{-2})	4.6 ± 0.1	4.02^c	2.6 ± 0.1	4.7 ± 0.1	3.5
Iodide	log K_0 (ml g^{-1})	5.0 ± 0.1	4.85 ± 0.07	2.93 ± 0.08		
	log K_3 (M^{-1})	3.8 ± 0.3	3.67^c	3.0 ± 0.1	3.7 ± 0.1	3.1
	log K_{34} (M^{-2})	6.4 ± 0.3	6.04^c	4.4 ± 0.1	5.6 ± 0.1	4.4

[a] Units of $\bar{K}_3$ and $\bar{K}_{34}$ in this column are kg resin mole^{-1} and (kg resin)^2 mole^{-2} respectively.

[b] The values in this column have been calculated from the values in the previous column by converting the concentration units from moles/kg resin to moles per liter (internal solution). The conversion factor by which K_3 or $K_{34}^{1/2}$ are multiplied, 0.25, has been obtained from the water content of the equilibrated resin([illegible]).

[c] From reference (11).

Once the values of $\bar{K}_3$ and $\bar{K}_{34}$ have been obtained, and assuming that they are independent of the ionic strength of the external solution, values of K_3 and K_{34} for total concentrations $C = 0.3$ and 3.0 M may be obtained from Equation (5) by a reverse process to the above. The constants thus obtained are shown in Table 1.

DISCUSSION

Although the mercury halide system is relatively simple, there being only three complex species in each phase, the expression for the distribution coefficient(5) turns out to be rather complicated, and did not permit an independent determination of all five required parameters. This makes doubtful the possibility of using the constant ionic medium method independently on much more complicated systems. On the other hand, the method is highly valuable for obtaining the stability constants for the resin phase.(5) Equation (5) may, of course, be generalized by considering other species.

It is interesting to compare constants found for various ionic media. The parameter K_3 for adding a singly charged halide anion to neutral mercury halide to form the singly charged complex anion involves a ratio of activity coefficients of univalent ions, and the activity coefficients of the uncharged molecule

$$K_3 = (\mathrm{HgX_3^-})/(\mathrm{HgX_2})(\mathrm{X^-}) = K_3^{\mathrm{therm}}\, y_{\mathrm{HgX_2}}\,(y_{\mathrm{X^-}}/y_{\mathrm{HgX_3^-}}) \tag{7}$$

where K_3^{therm} is the thermodynamic equilibrium constant which is of course independent of the medium concentration, and the y's are molar activity coefficients. If the ratio is taken as approximately unity, or at least as invariant with medium concentration, the effect of changing the ionic strength of the perchlorate medium should be the same for K_3, as for K_0, the constant for transferring the neutral mercury halide to the invariant resin Indeed, the difference log K_0 − log K_3 is found to be approximately independent of the ionic strength The variation of K_0 (or K_3) with ionic strength, however, is opposite to what is expected from the salting effect of sodium perchlorate on the mercury halides, measured by extraction with benzene[19] There a salting constant of +0 14 was found, independent of the halide used, but here the salting constants are approximately −0 3 and show some variation with the halide No reason for this discrepancy is directly evident Another point to be noted is the stepwise formation of the anionic species in the resin phase, as shown by the magnitude of the constants $\bar{K}_3$ and $\bar{K}_{34}$ This behaviour at relatively low ligand concentration in the resin in presence of a large excess of perchlorate ions, is contrary to that found when only ligand ions are present in the resin[20] Although in the latter case the ligand activity varies also, because of electrolyte invasion, it is initially at such a high concentration that usually only a single anionic complex predominates in the resin

---

(18) L. G. SILLÉN, *Acta Chem. Scand.* **10**, 186 (1956).

For the cadmium bromide system it has been shown[5] that the stabilities of the complexes with one to three ligands are considerably enhanced in the resin phase compared to aqueous solutions The complex with four ligands, however, was approximately equally stable in both phases This has been connected[5] with the changes of the stability of the complexes with ionic strength, observed in aqueous solutions The ionic strength in the resin, approximately 12 M, is however quite outside the range of 1–3 M, on which the above conclusion is based, and additional factors may be important Examination of the values in Table 1 for the mercury halide systems shows that as the ionic strength increases, the chloride shows a pronounced minimum in the constants, the bromide a somewhat less pronounced minimum, while the iodide shows decreasing constants with no clear minimum An explanation for this trend may be sought in the competing action of the screening and dehydrating effects of the medium The first factor should be independent of the ligand, while for the second, the effect for the chloride, bromide and iodide should decrease in this order Thus for the more dehydratable chloride ligand, the complex formation in the resin should be enhanced as compared to aqueous solutions due to the highly dehydrating environment of the resin[21] (particularly in the perchlorate form) No such enhancement should occur with the relatively non-dehydratable iodide ion This is, in fact, confirmed by the data in Table 1.

Acknowledgements—The technical assistance of Mrs N Bauman and Miss S Yitshaki is gratefully acknowledged

---

[19] Y Marcus, *Acta Chem Scand* **11**, 329 (1957)

[20] I Eliezer and Y Marcus, *J Inorg Nucl Chem* **25**, 867 (1963)

[21] Y Marcus and D Maydan, *J Phys Chem* **67**, 983 (1963)

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 1471 to 1475. Pergamon Press Ltd. Printed in Northern Ireland

NOTE

Differential thermal analysis of some cyano and cyanonitrosyl iron complexes(1)

(*Received* 6 *May* 1963)

THE THERMAL decomposition of hexacyanoferrate (II) and (III) compounds and of certain cyanonitrosyl ferrates has been the subject of numerous investigations.(2–8) These early studies were made under a variety of conditions and thus report a variety of decomposition temperatures and products. Only recently has there been a report of a systematic study of several of these compounds using the techniques of differential thermal analysis.(9) As part of a general investigation in these laboratories of reactions leading to the formation of inorganic macromolecules, the thermal decomposition of a variety of cyano and cyanonitrosyl ferrates has been studied by differential thermal analysis (DTA) and a complementary technique, dynamic gas evolution (DGE).

EXPERIMENTAL

Apparatus

The DTA apparatus was constructed in these laboratories. A cell block was made from a cylindrical nickel rod (1.9 cm dia. by 6.3 cm length) with a face machined along the rod parallel to the long axis and two holes, perpendicular to the axis, drilled to accommodate Pyrex crucibles (1.4 cm dia. by 1.2 cm deep).

The block temperature was measured with a chromel-alumel thermocouple inserted into a hole drilled in the centre of the block perpendicular to the face. The differential thermocouple was of chromel-constantan, held in position by a detachable spacer bar mounted on centring pins. The block temperature was recorded with a Micromax S recorder, the differential temperature with a Sargent MR recorder.

Heating was furnished by a 750 W Hevi-Duty combustion tube furnace fitted with a Vycor tube (2.5 cm by 60 cm). A laboratory-built programmer insured that the temperature of the furnace could be increased at a uniform rate.

The technique of dynamic gas evolution is described elsewhere(10a, b) as is the detector unit and electrical circuitry.(11)

All studies were made with carefully dehydrated α-aluminum oxide as reference material, with a sample size of 0.3–0.5 g, a heating rate of 6°C/min and under a flow of dried oxygen-free nitrogen of 50 cm^3/min. The apparatus was calibrated against known lattice transition and melting point temperatures of ammonium nitrate, silver nitrate, potassium dichromate and sodium molybdate over the temperature range 32.2–687°C.

---

(1) Taken from the thesis submitted by A. F. GREENE, Jr. to the Graduate School of Western Reserve University in partial fulfillment of the requirements for the degree of Master of Science 1961.

(2) A. TERREIL, *C.R. Acad. Sci. Paris* **82**, 455 (1876).

(3) A. ETARD and G. BEMONT, *C.R. Acad. Sci. Paris* **99**, 972, 1024 (1884).

(4) V. CUTTICA, *Gazz. Chim. Ital.* **52**, 20 (1922).

(5) F. FICHTER and R. SUTER, *Helv. Chim. Acta* **5**, 396 (1922).

(6) L. HACKSPILL and H. J. PINCK, *Bull. Soc. Chim. (France)* **49**, 54 (1931).

(7) A. PERRET and A. GISLON, *Bull. Soc. Chim. (France)* **53**, 283 (1933).

(8) C. DUVAL, *Inorganic Thermogravimetric Analysis*, p. 404. Elsevier, Amsterdam (1953).

(9) G. B. SEIFER, (a) *Zh. Neorg. Khim.* **5**, 68 (1960); (b) *Ibid.* **7**, 482 (1962).

(10) (a) W. M. AYRES and E. M. BENS, *Anal. Chem.* **32**, 1374 (1960);
(b) W. W. WENDLANDT, *Anal. Chim. Acta* **27**, 309 (1962).

(11) H. R. FELTON and A. A. BUEHLER, *Anal. Chem.* **30**, 1163 (1958).

Reagents

All reagents were either obtained commercially in reagent grade purity or prepared in these laboratories

Lithium, sodium, calcium, and barium hexacyanoferrate (III) were prepared by reaction of silver hexacyanoferrate (III) and the desired metal chloride, lithium, potassium, and barium pentacyanonitrosylferrate (II) by the analogous reactions of silver pentacyanonitrosylferrate (II) Interestingly enough, ethanol and tetrahydrofuran, when added to effect crystallization, gave higher hydrates than when recrystallization was effected from water alone

ANALYSIS

Compound	Calculated (%)				Found (%)			
	Fe	Ca	Ba	H_2O	Fe	Ca	Ba	H_2O
$Li_3[Fe(CN)_6]\ 8H_2O$	14 82				14 70 14 93			
$Ca_3[Fe(CN)_6]_2\ 18H_2O$	12 86	13 85			12 72 12 82	13 58		
$Ba_3[Fe(CN)_6]_2\ 18H_2O$	9 61		35 50		10 08 10 10		35 45 35 65	
$Li_2[Fe(CN)_5NO]\ 4H_2O$	18 55			13 9	18 15 17 85			13 7
$Ba[Fe(CN)_5NO]\ 6H_2O$	12 12		29 77		12 39		29 35 29 97	

Turnbull's Blue was prepared by the method of WEISER *et al*[12] Excess water was removed by drying on the steam bath

DTA and DGE peaks

Peak temperatures on the differential thermal analysis curves were read at the first point of inflection after the curve departed from the base line Superimposition of the dynamic gas evolution curves onto the DTA curves clearly showed which DTA peaks were associated with gas evolution and which were due to lattice transformation and melting Further, the DGE peaks were frequently better resolved than the DTA peaks and allowed more exact determination of the decomposition temperatures

RESULTS

Complete results are shown in Table 1 and some representative DTA and DGE curves in Fig 1

Two results are immediately obvious First, water is removed at temperatures ranging from about 80 C to as high at 180°C, but for most compounds at about 100 C These reactions are endothermic Secondly, cyanogen is a common product from all these thermal decompositions and is evolved as the result of an exothermic reaction Since the formation of cyanogen from cyanide is an oxidation reaction, it seems reasonable to suggest that the metal is being reduced and that the compounds formed as thermal decomposition proceeds contain the metal in successively lower formal oxidation states

As a general rule, the iron (III) complexes decompose at a markedly lower temperature than the analogous iron (II) species, decomposition is thus to be associated with the ease of reduction of the metal ion and not with any intrinsic stability of the metal–cyanide bond Both the iron (II) and the

---

[12] H B WEISER, W O MILLIGAN and J B BATES, *J Phys Chem* **46**, 99 (1942)

TABLE 1 —THERMOLYSIS TEMPERATURES AND CHARACTERISTICS

Compound	DTA Peak Temp (°C)	DTA Peak Characteristics	Gaseous Products
$Li_3[Fe(CN)_6]\cdot 8H_2O$	148	endo, s	H_2O
	240	endo, m	
	266	exo, sp	C_2N_2
$Na_3[Fe(CN)_6]\cdot 2H_2O$	128	endo, s	H_2O
	280	exo, s sp	C_2N_2
$K_3[Fe(CN)_6]$	340	exo, vs, vsp	C_2N_2
$Ca_3[Fe(CN)_6]_2\cdot 18H_2O$	84	endo, sh	H_2O
	100	endo, s	H_2O
	150	endo, m	H_2O
	272	exo, m, b	C_2N_2
	318	endo, m b	C_2N_2
$Ba_3[Fe(CN)_6]_2\cdot 18H_2O$	68	endo sh	H_2O
	82	endo, sh	H_2O
	116	endo, s	H_2O
	216	exo s, sp	C_2N_2
	262	endo vb	C_2N_2
	(286)	(DGE peak maximum)	
$Na_4[Fe(CN)_6]\cdot 10H_2O$	88	endo, sh	H_2O
	116	endo, s	H_2O
	600	exo w vb	C_2N_2
$K_4[Fe(CN)_6]\cdot 3H_2O$	100	endo, s	H_2O
	588	endo, w, vb	C_2N_2
$Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$	148	endo s	H_2O, NH_3
	298	exo, sl	C_2N_2
	352	exo m	C_2N_2
	600	endo w b	C_2N_2
Turnbull's Blue $KFe[Fe(CN)_6]\cdot xH_2O$	100	endo, m, vb	H_2O
	196	exo, s b	C_2N_2
	290	endo, m b	C_2N_2
	324	exo, s, b	C_2N_2
	398	endo s	C_2N_2
	470	exo, w, sh	C_2N_2
	605	exo, s sp	N_2
Prussian Blue $KFe[Fe(CN)_6]\cdot yH_2O$	100	endo m vb	H_2O
	196	exo s, b	C_2N_2
	270	endo, m, b	C_2N_2
	324	exo, s, b	C_2N_2
	380	endo s	C_2N_2
	433	exo, w, sh	C_2N_2
	605	exo s sp	N_2

TABLE 1—(cont'd)

Compound	DTA Peak		Gaseous Products
	Temp (°C)	Characteristics	
$Li_2[Fe(CN)_5NO]\ 4H_2O$	86	endo, m	H_2O
	122	endo, s	H_2O
	294	endo, s	NO
	338	exo, sh	C_2N_2
$Na_2[Fe(CN)_5NO]\ 2H_2O$	158	endo, vs	H_2O
	309	endo, s	NO
	338	exo, sh	C_2N_2
$K_2[Fe(CN)_5NO]\ 2H_2O$	92	endo, sh	H_2O
	120	endo, s	H_2O
	286	exo, w	NO
	306	exo, s	C_2N_2
	639	endo, m	melting
$Ba[Fe(CN)_5NO]\ 6H_2O$	94	endo	H_2O
	180	endo	H_2O
	324	(DGE peak only)	NO
	334	exo, vs, sp	NO, C_2N_2
$K_3[Co(CN)_6]$	420	endo, w, b	C_2N_2
	559	endo, m, sp	l t
	665	exo w b	C_2N_2

Key endo = endothermic exo = exothermic w = weak m = medium s = strong
sp = sharp b = broad sh = shoulder v = very l t = lattice transition

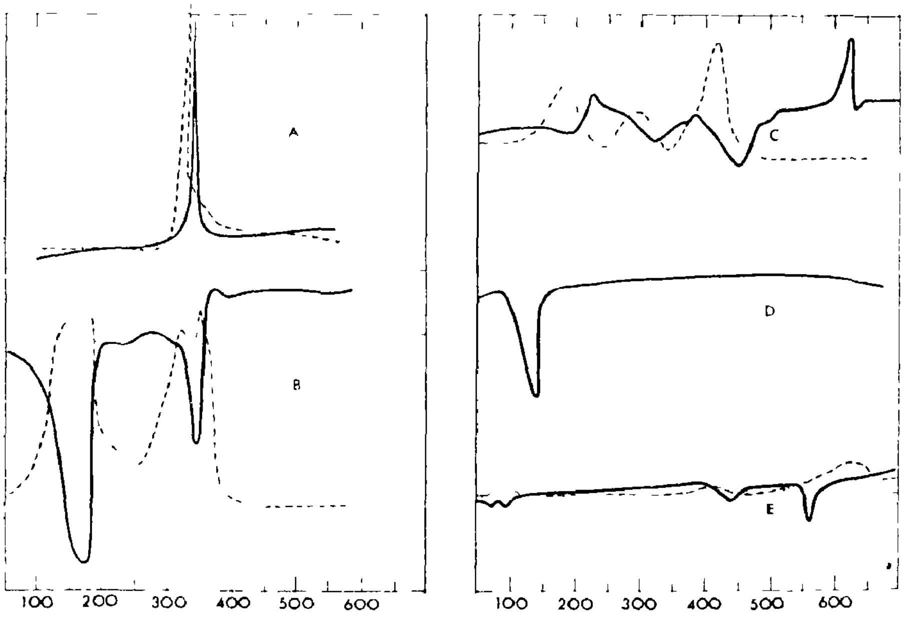


FIG 1 —Concurrent DTA and DGE curves of transition-metal cyano complexes
DTA —— DGE- - -
A $K_3[Fe(CN)_6]$ B $Na_2[Fe(CN)_5NO]\ 2H_2O$ C Turnbull's Blue D $K_4[Fe(CN)_6]\ 3H_2O$
E $K_3[Co(CN)_6]$

iron (III) complexes are high field-low spin species, the d^5 iron (III) is readily reduced whereas the d^6 iron (II) species is resistant to further reduction This resistance of high field d^6 cyano complexes to thermal decomposition is expected and observed in potassium hexacyanocobaltate (III) It should also be noted that the strong, sharp exothermic decomposition observed for both Turnbull's Blue and Prussian Blue at 605° corresponds to the ultimate decomposition to iron carbide, carbon and nitrogen as reported by SIEFER(10b)

The cyanonitrosyl complexes decompose first to lose nitric oxide, then at higher temperatures cyanogen is evolved Formally, iron may be considered to exhibit a +2 oxidation state in these complexes, elimination of nitric oxide thus involves an oxidation of iron to a 3 state and cyanogen formation a reduction back to iron (II) The comparatively low temperatures (ca 300) for cyanogen evolution are consistent with this interpretation

Preliminary weight loss studies, infrared examination of the decomposition residues, and the generally intractable nature of these solids indicate that stable, polymeric materials involving metal-cyanide-metal bridging are formed Characterization of these residues is now in progress as is further study of cyano and cyanonitrosyl complexes of molybdenum, chromium, and vanadium

Acknowledgement –This work has been supported in part by the Office of Naval Research

Department of Chemistry
Western Reserve University
Cleveland 6 Ohio

M M CHAMBERLAIN
A F GREENE, JR

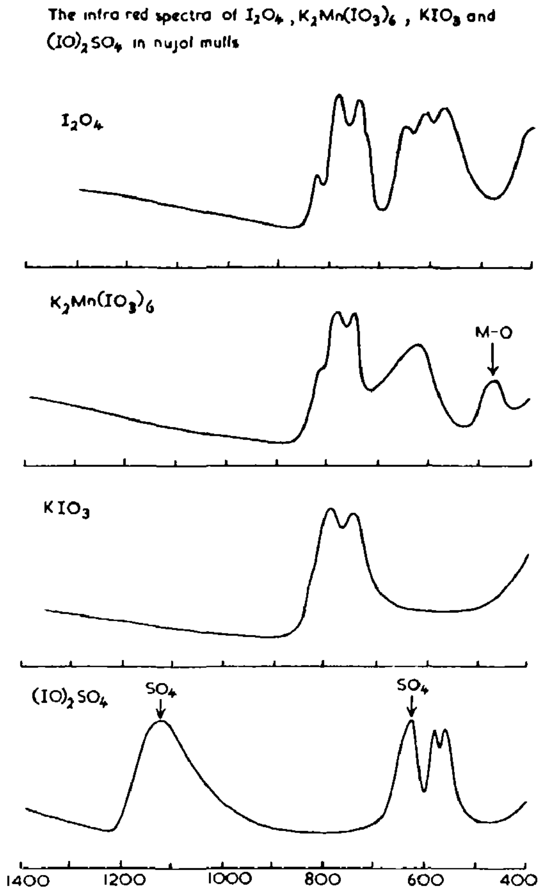


FIG. 1. The infra-red spectra of I_2O_4, $K_2Mn(IO_3)_6$, KIO_3 and $(IO)_2SO_4$ in Nujol mulls.

(3) Completely isoelectronic compounds have very similar vibration frequencies. Changes in charge only affect these slightly. Now molecular TeO has a fundamental vibration frequency of 796 cm^{-1} and so we might expect for the isoelectronic IO$^+$ a vibration frequency of about 800 cm^{-1} or a little higher. In iodosyl sulphate and selenate, and in iodine dioxide we found that the only absorption attributable to the IO group occurred in the frequency range 553–658 cm^{-1}. This is considerably lower than any I–O stretching frequency let alone the frequency to be expected of IO$^+$.

Department of Chemistry
Victoria University
Wellington, New Zealand

W. E. DASENT

University Chemical Laboratory
Cambridge, England

T. C. WADDINGTON

A change in radioactive product distribution for recoil tritium reactions in the solid phase at -196°C$^{(1)}$

Most of the reactions of recoil tritium atoms with organic molecules have been shown to occur while the atom still possesses excess kinetic energy from the nuclear reaction.$^{(2)}$ This additional energy at

---

(1) This research is supported by A.E.C. Contract No. AT-(11–1)-407.

(2) *Chemical Effects of Nuclear Transformation* Vol. 2. International Atomic Energy Agency, Vienna 1961. R. WOLFGANG *et al.* p. 83 and p. 99. F. S. ROWLAND *et al.* p. 67.

J Inorg Nucl Chem, 1963 Vol 25 pp 1477 to 1481 Pergamon Press Ltd Printed in Northern Ireland

THE NATURE OF THE OXYGEN-BRIDGE BOND IN CO-ORDINATION COMPOUNDS*

B Jeżowska-Trzebiatowska and W Wojciechowski
Department of Inorganic Chemistry University of Wrocław

(*Received* 27 *November* 1962, *in revised form* 1 *May* 1963)

The electronic structure of oxygen enables it to bind other atoms by various types of bonds, ionic or covalent, with the help of single electrons, or to form π- and σ-donor bonds. Thus the oxygen bridge bonds are particularly stable when the d and f-orbitals of the attached atoms are accessible The oxygen bridge often leads to a change in the electronic structure of the attached atoms This change may be confirmed experimentally only for paramagnetic atoms In such cases the paramagnetism of the metal-atoms bridged by the oxygen disappears partly or completely In the first series of transition elements the disappearance of paramagnetism has been confirmed in the products of the hydrolysis of iron(1) and in the μ oxo bis pentammine chromium (III) chloride (2) In the second transition series it has been observed for molybdenum (V) in the so-called "molybdenum blue,(3) in ruthenium (IV) in oxochlororuthenate(4) and probably in our recently reported oxygen bridged complex of technetium (IV) (5)

The most convincing example of metal atom interaction with the oxygen bridge has been discovered in the third series of transition metals in rhenium (IV) (6) We have found diamagnetism not only in oxochlororhenate, which is analogous to oxochlororuthenate, but also in a whole group of rhenium (IV) complexes with organic ligands (7) Rhenium complexes are therefore the most convenient group in which to investigate the nature of the oxygen bridge between metal atoms One unpaired $d\epsilon$ electron on each metal atom may be assumed for the treatment of oxochlororhenate We have treated this structure as monoelectronic which permitted us to find the energy and length of the bond by a valency bond method, assuming the group Re—O—Re to be linear We have calculated(8) the bond length and the energy for the following structures

Structure	Bond length (Å)	Bond energy (k cal/mole)
$Re^{3+}—O^{0}—Re^{3}$	1 75	8 0
$Re^{2}—O^{2+}—Re^{2}$	1 98	7 0
$Re^{0}—O^{2}—Re^{0}$	1 82	7 3

---

* Paper presented at the 7th Congress of Co-ordination Chemistry, Stockholm, 1962

(1) L N Mulay and P W Selwood *J Amer Chem Soc* 77, 2693 (1955)

(2) A Earnshaw and J Lewis, *J Chem Soc* 396 (1961) B Jeżowska-Trzebiatowska and W Wojciechowski, *Theory and Structure of Complex Compounds* Symposium Wrocław 1962 Pergamon Press London, WNT-Warszawa in press

(3) L Soccani and R Cini *J Amer Chem Soc* **76**, 4239 (1954)

(4) D P Mellor *J Roy Soc N S Wales* **77**, 145 (1943)

(5) B Jeżowska-Trzebiatowska J Ziołkowski and M Baluka In press

(6) B Jeżowska-Trzebiatowska and S Wajda *Bull Acad Polon Sci* **2**, 249 (1954)

(7) B Jeżowska-Trzebiatowska and S Wajda, *Bull Acad Polon Sci* **6**, **217** (1958) **9**, 57 (1961) B Jeżowska-Trzebiatowska, S Wajda and W Wojciechowski *Bull Acad Polon Sci* **9**, 65 (1961), B Jeżowska-Trzebiatowska and Wojciechowski *Bull Acad Polon Sci* **9**, 685 (1961)

(8) B Jeżowska-Trzebiatowska and W Wojciechowski *Bull Acad Polon Sci* **11**, 699 (1961)

The value obtained by MORROW by X-ray diffraction is 1 86 Å (private communi tion) and is near that, calculated for the third structure, supposing double bo between the oxygen and rheniums and 40 per cent covalent bonds between the rheni and chlorine

Oxochlororhenate $K_4Re_2OCl_{10}$ has D_{4h} symmetry and each rhenium atom C symmetry like the ruthenium complex whose molecular orbitals were deduced by DUNITZ and ORGEL (9) In our calculations we have also taken into account the symmetry of the oxygen C_2 From the symmetry of the atomic orbitals the following combinations are possible

D_{4h}				
	a_{1g}	d_{z^2}	s	
	b_{1g}	$d_{x^2-y^2}$		
	a_{2u}	p_z		
	b_{2g}	d_{xy}		
	e_u	p_x	p_y	
	e_g	d_{xz}	d_{yz}	
C_{4v}				
	a_1	d_{z^2}	s	p_z
	b_1	$d_{x^2-y^2}$		
	b_2	d_{xy}		
	e	d_{xz}	p_x	
		d_{yz}	p_y	
C_2				
	a	s	p_z	
	b	p_x	p_y	

leading to the following sequence of molecular orbitals (10)

$$E_g{}^b \quad E_u \quad A_{1g} \quad A_{2u} \quad E_g{}^a$$

Ten electrons of the Re—O—Re nucleus are placed in the $E_g{}^bE_uA_{1g}$ orbitals causing diamagnetism This scheme may be applied to all complexes of this symmetry, D_{4h} and, hence to oxochlororuthenate $K_4Ru_2OCl_{10}$ with a d^4 electronic structure as well as to the μ oxo bis pentammine chromium (III) chloride with a d^3 electronic structure

The scheme fails for iron (III) and molybdenum (V) complexes where the nucleus may have a different structure, e g $\mathrm{Me}{\scriptstyle\genfrac{}{}{0pt}{}{\mathrm{OH}}{\mathrm{OH}}}\mathrm{Me}$

Although the scheme explains the properties of the Re(IV) complexes with organic acids it is not possible to include these compounds in this category In these each rhenium atom is surrounded by fine oxygens of carboxyl or hydroxo groups besides the oxygen bridge, and each of them may compete in π-bond formation The π-bo resonance strengthens the whole complex Under these conditions the molecul orbitals must be different from those in oxochlororhenate

---

(9) J D DUNITZ and L E ORGEL, *J Chem Soc* 2594 (1953)

(10) B JEZOWSKA-TRZEBIATOWSKA and W WOJCIECHOWSKI, Sympozjum "*Teoria i struktura zwia* *kompleksowych*, Wroclaw (1962), Pergamon Press, London, WNT, Warszawa in press

The problem of the disappearance of paramagnetism in the Cr(III) complexes is more complicated than in oxochlororhenate Two pairs of complexes occur (11)

(1) μ hydroxo bis pentammine chromium (III) chloride $(Cr_2OH)(NH_3)_{10}Cl_5$, and μ oxo bis pentammine chromium (III) chloride $(Cr_2O)(NH_3)_{10}Cl_4$

(2) μ hydroxo pentammine aquo tetrammine chromium (III) chloride $(Cr_2OH)(NH_3)_9(H_2O)Cl_5$, and μ hydroxo pentammine hydroxo tetrammine chromium (III) chloride $(Cr_2OH)(NH_3)_9OHCl_4$

Three of these complexes exhibit a paramagnetism corresponding to one electron spin per chromium atom The results(12) of our measurements coincide with the data obtained by LEWIS and ERNSHAW (2)

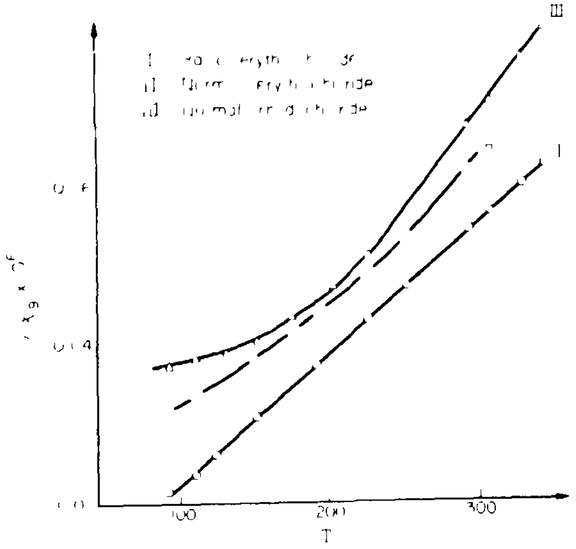


FIG 1 —I-basic eythrochloride, II normal eythrochloride, III normal rhodochloride

μ Oxo bis pentammine chromium (III) chloride shows a small paramagnetism decreasing with temperature and at 125 K changing to diamagnetism The temperature dependence may be expressed as follows $\chi_g = 0.88\chi ([T^2/\theta^2) - 1]$

The investigation of the paramagnetic resonance spectra of the three binuclear Cr(III) complexes gives the following half width line and g values at room and liquid air temperatures

TABLE 1

	μ_{eff} in BM	g' 293 K	g' 84 K
μ hydroxo bis pentammine chromium III chloride	1.85	1.986	
μ hydroxo pentammine aquo tetrammine chromium III chloride	2.26	2.009	2.04
μ hydroxo pentammine hydroxo tetrammine chromium III chloride	2.3	1.993	2.01

---

(11) K WILMARTH, H GRAFF and T GUSTIN, *J Amer Chem Soc* **78**, 2683 (1956)

(12) B BEZOWSKA-TRZEBIATOWSKA and W WOJCIECHOWSKI *Bull Acad Polon Sci* In press

Only very weak π-bonds between the ligand and chromium (III) atoms occur in the μ-hydroxo pentammine aquo tetrammine chromium III chloride, μ-hydroxo pentammine hydroxo tetrammine chromium III chloride and in the μ hydroxo bis pentammine chromium III chloride The bonds may be interpreted as arising from the joint action of the oxygen and nitrogen with the metal atoms

The μ oxo bis pentammine chromium (III) chloride does not show a paramagnetic absorption even in liquid air Thus the electrons must be in molecular orbitals, as in the oxochlororhenate The difference between these two complexes arises because one involves 5*d* orbitals which lie outside the 3 *d* orbitals concerned in the other Thus, there exists in the heavy metals a greater possibility of stable π-bond formation In the μ oxo bis pentammine chromium (III) chloride the A_{1g} and A_{2u} levels are close to each other and there is a possibility of thermal excitation The result is a small paramagnetism of this compound at higher temperatures When chromium atoms are bridged by an OH or H_2O group, no molecular orbitals are formed and the π-bonds are weak and only cause splitting of the T_{2g} orbitals into a singlet and a doublet levels, which leads to paramagnetism corresponding to one electron per chromium This configuration is revealed in the absorption spectra Oxochlororhenate and μ oxo bis pentammine chromium (III) chloride show two split absorption bands each in a similar region of the spectrum (13,14)

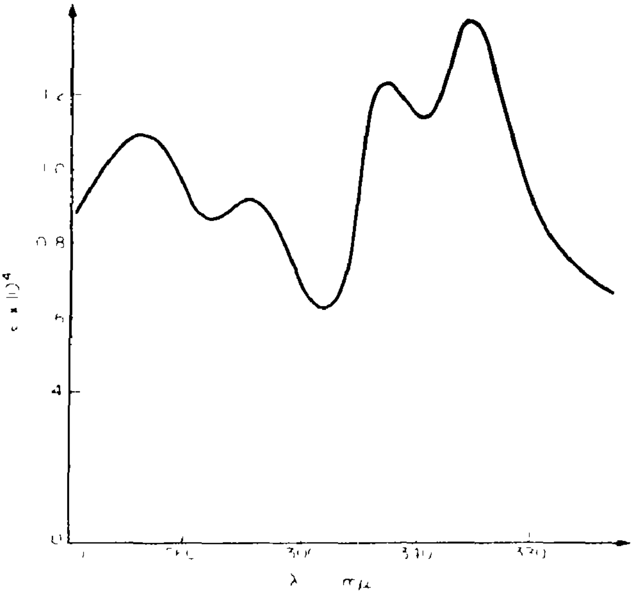


FIG 2a —Absorption spectrum of $K_4Re_2OCl_{10}$

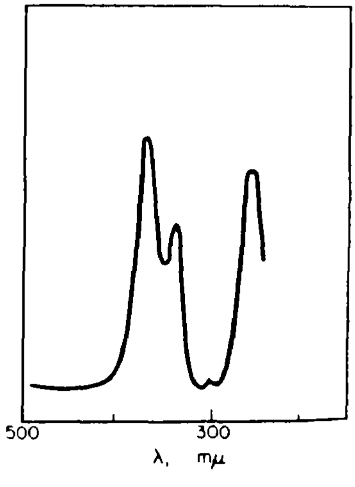


FIG 2b —The reflexion spectra of basic rhododithionate $[(NH_3)_5CrOCr(NH_3)_5]^{4+}$

The band in the near ultra-violet may be ascribed to transitions within the energy levels of the Me—O—Me nucleus, from orbital A_{2u} to E_g^a and from orbitals A_{1g} to [illegible], while the band in the far ultraviolet corresponds to transitions from the ligands orbitals to the orbitals (A_{2u} or E_g^a) of the nucleus Me—O—Me In oxochlororhenate we have also found two bands, but they are not split.(15)

---

(13) B JEZOWSKA-TRZEBIATOWSKA and H PRZYWARSKA, *Bull Acad, Polon Sci* **9,** 679 (1961)

(14) C E SCHAFFER, *J Inorg Nuclear Chem* **8,** 149 (1958)

(15) B JEZOWSKA-TRZEBIATOWSKA and R GROBELNY, to be published

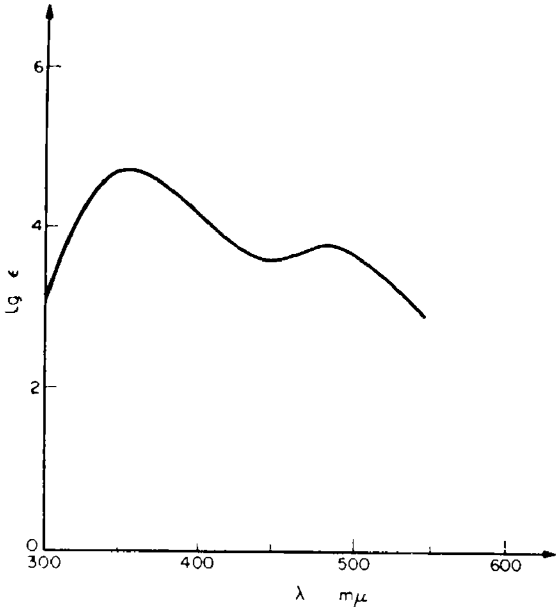


FIG 3 —Absorption spectrum of $K_4Ru_2OCl_{10}$

The disappearance of the splitting may be due to the filling of the orbital A_{2u}

The absorption band in the near ultra-violet may be considered as characteristic of the oxygen-bridge, and as proof of common molecular orbitals in Me—O—Me system

On the basis of the above investigations and theoretical discussion it may be accepted that in an Me—O Me system, with accessible *d* levels on the metals, molecular orbitals are formed and in such case an oxygen atom may be treated as a real bridge bond for other atoms

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 1483 to 1486. Pergamon Press Ltd. Printed in Northern Ireland

COMPLEXES OF TUNGSTATE AND MOLYBDATE IONS CONTAINING TWO ORGANIC LIGANDS

D. H. BROWN and J. D. McCALLUM
Chemistry Department, The Royal College of Science and Technology, Glasgow C.1

(*Received* 4 *April* 1963, *in revised form* 21 *May* 1963)

Abstract—Tungstate and molybdate ions complex with 1,2-dihydroxyphenols and with α-hydroxy carboxylic acids. The formation of the former type of complex can be detected by the change in spectrum of the solution and of the latter, if optically active organic acids are used, by a marked increase in the optical rotation. Complexes containing both 1,2-dihydroxyphenol and α-hydroxy-carboxylic acid ligands with molybdate or tungstate ions have been detected in solution and the stoicheiometry ascertained. The changes in optical rotation and ultra-violet spectra associated with these complexes are discussed.

TUNGSTATE and molybdate ions complex readily with compounds containing a 1,2-dihydroxybenzene grouping.[1,2] These complexes are strongly coloured, red for molybdate and yellow for tungstate. The stoicheiometry of these complexes in solution is nearly always 2 : 1, organic ligand to metal, although on precipitation a 1 : 1 complex is generally obtained. In the following investigation 1,2-dihydroxybenzene 3,5-disulphonic acid was mainly used because of its fairly high solubility in water and also because it is relatively more stable than catechol to air oxidation in neutral solution. However, catechol and 3,4-dihydroxybenzoic acid gave similar results when tested. The optically active α-hydroxycarboxylic acids used were D-tartaric acid and L-mandelic acid. They give 1 : 1 and 2 : 1 acid : metal complexes respectively.[3,4]

The purpose of this present investigation was to see if an organic acid ligand could replace one of the 1,2-dihydroxybenzene 3,5-disulphonic acid ligands and to relate the different changes obtained in optical rotation and ultra-violet spectra of the complexed molybdate and tungstate ions.

RESULTS

The variation in optical rotation (20 cm tube, sodium D light) with pH of a solution 0·04 M in D-tartaric acid and sodium tungstate and 0·08 M in 1,2-dihydroxybenzene 3,5-disulphonic acid ('Tiron') is shown in Fig. 1. The variation in optical rotation with pH of a sodium D-tartratotungstate solution is shown for comparison. Also given are the graphs for the corresponding molybdate solutions. In this case due to the intense colour, the solutions were diluted by a factor of eight.

Fig. 2 shows the graph of optical density against pH of a solution 0·004 M in sodium tungstate and D-tartaric acid and 0·008 M in 'Tiron'. The curve for a solution of the 1 : 2-tungstate to 'Tiron' complex is given for comparison. The graphs for the corresponding molybdate solutions are also shown.

Using equimolar solutions of D-tartratotungstate and 'Tiron', a plot of optical density at 425 mμ against mole fraction of D-tartratotungstate showed the stoicheiometry of the complex to be 1 : 1. All the solutions were adjusted to pH 4·2. A similar result was obtained using D-tartratomolybdate in place of D-tartratotungstate.

---

[1] L. FERNANDES, *Gazzetta*, **55**, 424 (1925).
[2] D. H. BROWN, *J. Inorg. Nucl. Chem.* **17**, 146 (1961).
[3] M. J. BAILLIE and D. H. BROWN, *J. Chem. Soc.* 3691 (1961).
[4] D. H. BROWN, *J. Chem. Soc.* 1961, 4732.

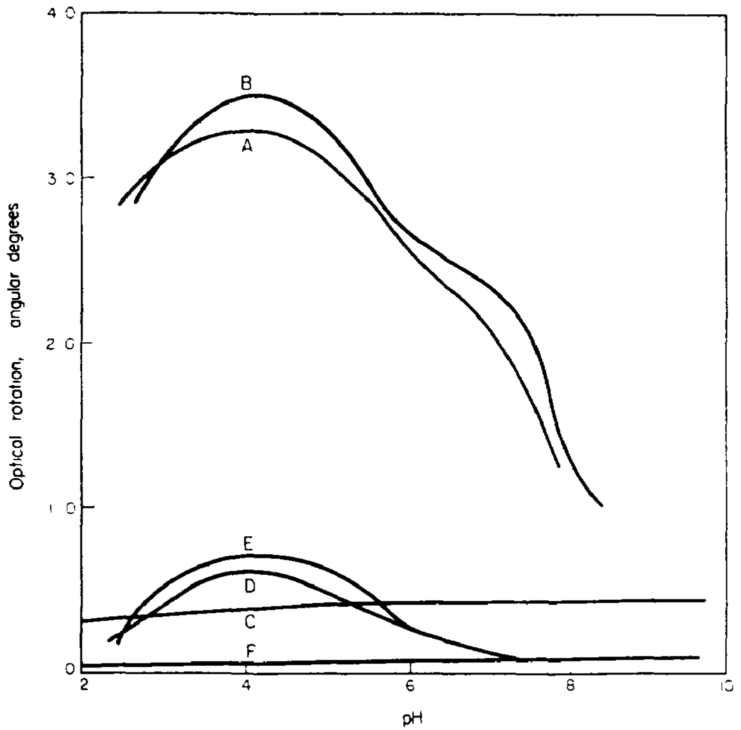


FIG 1 —Optical rotation plotted against pH for
A 4 × 10⁻² M sodium tungstate and D-tartaric acid and 8 10⁻² M
Tiron
B 4 × 10⁻² M sodium tungstate and D-tartaric acid
C 4 × 10⁻² M D-tartaric acid
D 5 × 10⁻³ M sodium molybdate and D-tartaric acid, and 1 10⁻² M
Tiron
E 5 × 10⁻³ M sodium molybdate and D-tartaric acid
F 5 10⁻³ M D-tartaric acid

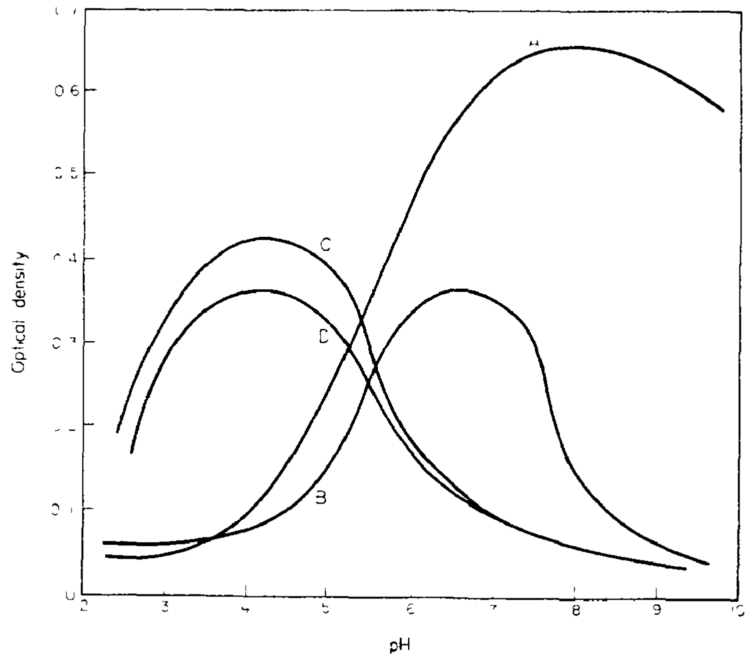


FIG 2 —Optical density at 425 mμ plotted against pH for
A 4 10⁻³ M sodium tungstate and 8 10⁻³ M Tiron
B 4 10⁻³ M sodium tungstate and D-tartaric acid, and 8 10⁻³ M
Tiron
C 4 10⁻⁴ M sodium molybdate and 8 × 10⁻⁴ Tiron
D 4 10⁻⁴ M sodium molybdate and D-tartaric acid, and 8 10⁻⁴ M
Tiron

The above experiments were repeated using L-mandelic acid in place of D-tartaric acid and similar results were obtained The optical rotation of L-mandelatotungstate was only slightly decreased on the addition of 'Tiron' and the optical densities were almost identical to those recorded in Fig 2 Again a Job's plot suggested a 1 1 Tiron. L-mandelatotungstate complex

The effect on the optical rotation, at constant pH, of D-tartratotungstate solutions, of other added compounds was also examined The graphs of optical rotation against

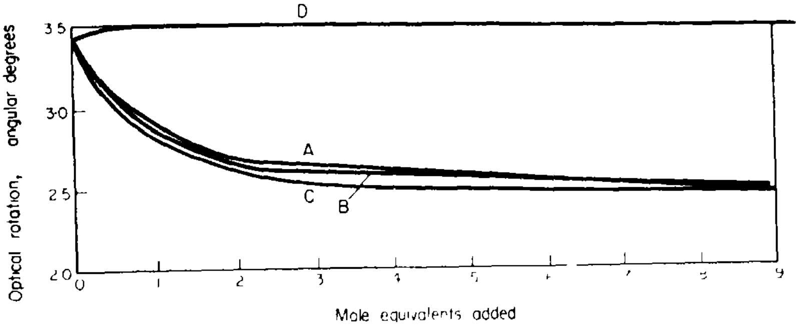


FIG 3 -Optical rotation plotted against mole equivalent of added compounds, for solutions 4 × 10^{-4} M in D-tartratotungstate plus (a) tiron (b) oxalic acid (c) mandelic acid and (d) sodium chloride All at pH 4 2

mole equivalents of added tiron, oxalic acid, sodium chloride, and mandelic acid are shown in Fig 3

The ultra-violet spectra of a number of the solutions described above were taken on an Optika Recording Spectrophotometer The results obtained were inconclusive as the very intense charge transfer peaks ($\pi \rightarrow \gamma_3$) for MoO_4^{2-} and WO_4^{2-} ions at approximately 44,000 and 50,000 cm^{-1} tended to mask the other peaks However for the Tiron-tungstate and Tiron-D-tartratotungstate complexes an extra peak was obtained about 32,000 cm^{-1} ($\epsilon \approx 9{,}000$) whereas for the corresponding molybdate complexes only a broad peak with a long tail extending into the visible was found

DISCUSSION

The variations in optical rotations, from Fig 1, of D-tartratotungstate and D-tartratomolybdate solutions with pH are little affected by the addition of Tiron Also, from Fig 2, the variation in optical density of D-tartratomolybdate solutions with pH is only slightly altered Since the optical rotation of D-tartratomolybdate solutions and the optical density of Tiron-molybdate solutions vary directly with the concentration of the complexes then the above results suggest that a molybdate complex is being formed containing both D-tartaric acid and Tiron molecules The Job's plot confirms the stoicheiometry of the complex as 1 1 1-molybdate D-tartaric acid Tiron Thus it appears that the D-tartaric acid replaces one Tiron molecule in the original complex

$$MoO_4[C_6H_2(OH)_2(SO_3)_2]_2^{6-} + C_4H_6O_6 \rightleftharpoons MoO_4[C_6H_2(OH)_2(SO_3)_2][C_4H_6O_6]^{4-} + C_6H_2(OH)_2(SO_3)_2^{2-}$$

This equilibrium could not easily be reversed as even with considerable excess of Tiron present (fortyfold excess), no apparent replacement of tartaric acid could be detected by optical rotation measurements The plot of optical density against pH for the tungstate–D-tartaric acid–Tiron complex solution shows a much lower maximum than does the parent tungstate–Tiron complex The possible reason for this will be discussed later in this paper

The ultra-violet spectra of the tungstate–Tiron and the tungstate-Tiron–D-tartaric acid solutions and the corresponding molybdate solutions are difficult to interpret The colour of the molybdate solutions is due to the long tail into the visible, although the first broad peak is just above that due to Tiron itself (at 34,000 cm^{-1}) This spectrum could be a combination of two Gaussian curves - the first due to Tiron and the second due to a charge transfer (mainly ligand → metal) at about 29,000 cm^{-1} The corresponding tungstate solutions show a broad peak about 32,000 cm^{-1} This again could be a combination of two Gaussian curves– the first due to Tiron and the second around 31,000 cm^{-1} due to charge transfer This order is as expected since Mo (VI) is a stronger oxidising agent than W (VI). If catechol is used, the optical density with molybdate ion is more intense than with Tiron Thus the electron withdrawing effect of the sulphonic acid groups in Tiron is reflected on the bond between ligand and metal Since no colour is produced in complexing MoO_4^{2-} and WO_4^{2-} ions with aliphatic polyalcohols like mannitol, it seems likely that the benzene rings are involved in the production of colour

The change in optical rotation of the D-tartaric acid on complexing is obviously related to the nature of the bond formed between it and the molybdate or tungstate ions From previous work it appears that the complexing group is the C O group (3) From the above experimental data it seems (i) that molybdate ion causes a greater change in optical rotation than does tungstate ion, (ii) that the addition of Tiron, oxalic acid or mandelic acid causes a decrease in optical rotation, and that (iii) the addition of sodium chloride causes a slight increase in optical rotation The most obvious explanation of these facts is that the change in optical rotation is due to the electron shift on the complexing carbonyl group the greater the electron transfer to the metal, the greater the change in optical rotation Thus, in agreement with the spectral data above, the Mo (VI) complexes with D-tartaric or mandelic acids should have higher optical rotations than the corresponding W (VI) complexes Also if the electron density on the metal ion is increased by the addition of other electron donating ligands, such as oxalic acid and Tiron, then the optical rotation should be decreased, as is found The increase in optical rotation in the presence of excess sodium chloride ion is probably due to the formation of ion pairs or aggregates with sodium ions and the complexed Mo (VI) and W (VI) anions, thus increasing the electron withdrawal from the carbonyl groups.

In Fig 2, the optical density of the tungstate–tiron complex is reduced on the addition of D-tartaric acid This is not the case with the corresponding molybdate solutions A possible reason for this is that at the pH where Tiron complexes most strongly, around pH7, the complexed tartaric acid is ionized This will increase the negative charge on the complex anion and so the charge transfer from Tiron to W (VI) will be inhibited and the corresponding charge transfer peak decreased in intensity, giving an apparent decrease in colour The molybdate–tiron complex on the other hand, appears to be formed around pH 4 as does the molybdate-tartaric acid (un-ionized) complex Thus the optical density is only slightly decreased the time of reaction permits high probabilities of reaction in collision, as evidenced primarily by the failure of free radical scavengers to suppress these reactions and suggests that the temperature of the target material is of only secondary importance in such reactions No temperature dependence of the radioactive product distribution from unscavengeable reactions has been demonstrated, although not many direct comparisons have been performed [3,4]

We have recently performed a series of experiments in which recoil tritium atoms from the $Li^6(n, \alpha)T$ reaction have been allowed to react with the same parent molecule *trans*-butene-2 at three different temperatures under otherwise similar conditions The results from the experiments in the liquid phase at 20°C and −78°C are very similar but those performed in the solid phase at −196°C show substantial changes in the quantitative yields of several products as shown in Table 1

TABLE 1 DISTRIBUTION OF RECOIL TRITIUM ACTIVITY IN *trans*-BUTENE-2-LiF MIXTURES AT THREE DIFFERENT TEMPERATURES
(Yields relative to parent = 100)

Product	Approximate temperature													
	20°C						−78°C				−196°C			
Exp Number	88		140		141		143		161		162		163	
	100		100		100		100		100		100		100	
	5.3	0.5	6.7	1.5	5.5	0.2	6.1	0.8	5.7	0.7	5.2	0.8	3.9	0.7
	17.0	0.8	21.7	1.5	17.4	0.9	25.4	0.9	23.4	0.8	22.3	0.8	20.3	0.9
	32.8	0.8	23.4	1.3	22.0	1.6	28.6	0.8	26.6	0.8	66.0	1.1	63.9	1.2
	(5	1)	7.1	1.5	6.8	1.1	5.1	0.8	4.0	0.7	1.5	0.7	1.3	0.4
	16.5	0.6	17.0	1.4	15.1	0.9	17.3	0.7	16.0	0.6	6.1	0.6	4.2	0.5
HT	191	4	163	6	176	4	187	4	184	4	158	3	153	3
CH_3T	4.2	0.4	3.7	0.9	1.9	0.5	3.8	0.4			2.9	0.4	2.1	0.4

The most significant variations are the decrease in $CH_3CH=CHT$ and the increase in n-C_4H_9T at −196°C from the other recorded values These radioactivity products result primarily from the reaction sequence (1) to (3)

$$T^* + CH_3CH=CHCH_3 \longrightarrow CH_3CHCHTCH_3^* \quad (1)$$
$$CH_3CHCHTCH_3^* \longrightarrow CH_3CH=CHT + CH_3 \quad (2)$$
$$CH_3CHCHTCH_3^* \longrightarrow CH_3CH_2CHTCH_3 \quad (3)$$

The probable route for most of reaction (3) is through the collisional deexcitation of the excited *sec*-butyl radicals, with subsequent chemistry leading to the n-C_4H_9T (e g disproportionation, hydrogen abstraction, etc) The change in phase from gas to liquid results in a decreased yield of (2) as expected from the large increase in collision rate in the liquid phase,[5] although the radical decomposition reaction persists in easily measurable yield [6] Reaction (2) only proceeds in the condensed phases if the radical has been formed through the reaction of a tritium atom with much more than thermal energy [7] The n-C_4H_9T, however, can result from the addition reactions of both thermal and hot tritium atoms, and cannot be readily separated into the two contributions

Several effects may contribute to the observed diminution in $CH_3CH=CHT$ yield at the lowest temperature *Trans*-butene-2 is a solid at −196 C, and a liquid at the other two, and the decrease most probably results from an increased efficiency of energy removal by the solid lattice relative to

---

[3] W J HOLT, Jr and F S ROWLAND, *J Amer Chem Soc* **79**, 4867 (1957)

[4] M EL-SAYED, P J ESTRUP and R WOLFGANG, *J Phys Chem* **62**, 1356 (1958)

[5] E K C LEE and F S ROWLAND, *J Amer Chem Soc* **84**, 3085 (1962)

[6] E K C LEE and F S ROWLAND, *J Chem Phys* **36**, 554 (1962)

[7] R F HARRINGTON, B S RABINOVITCH and M R HOARE, *J Chem Phys* **33**, 744 (1960), (and previous papers by B S RABINOVITCH)

J. Inorg. Nucl. Chem. 1963. Vol. 25. pp. 1487 to 1490. Pergamon Press Ltd. Printed in Northern Ireland

THE EFFECT OF CO-ORDINATION ON THE REACTIVITY OF AROMATIC LIGANDS—IX

SOME REACTIONS OF THE OPTICALLY ACTIVE ARSENIC (V)-CATECHOL COMPLEXES

T. H. LARKINS, JR. and M. M. JONES
Department of Chemistry, Vanderbilt University, Nashville, Tennessee

(*Received* 9 *May* 1963; *in revised form* 17 *June* 1963)

Abstract—A study had been made of the bromination and diazocoupling of optically active forms of the complexes of arsenic acid with catechol and 3-methylcatechol. The use of optically active forms provides a test of the lability of the complex under the conditions of the reactions. The retention of optical activity in the products of these reactions indicates that the reactions involve the complex itself, and not some ligand species which is momentarily dissociated.

ONE of the problems common to all investigations of the reactivity of co-ordinated species is that of assuring the coordination of the species whose reactivity is examined. In earlier studies in this laboratory,(1–3) complexes were used which were presumably inert on the basis of either reactivity towards disruptive reagents or a reluctance to undergo ligand exchange reactions. In the present study optically active complexes have been used to provide an internal criterion of lability. This method has been used earlier by COLLMAN and his co-workers(4) in the study of the reactivity of aliphatic ligands. The presumption being that for any reaction in which the optical activity is retained, *no ligand dissociation has occurred*. In the present study, we have examined the bromination and diazo-coupling of optically active arsenic (V) complexes with two aromatic 1,2-dihydroxy compounds. The reaction of phenols with bromine is quite vigorous and such reactions often lead to appreciable amounts of by-products which arise from the concurrent oxidation of the phenol. For coupling with diazonium salts, the phenolate anions are much more reactive than the phenols themselves. The complexes studied here contained phenolate anions as ligands and would be expected to couple rapidly with diazonium salts, unless the charge change was more than neutralized by the proximity of the highly charged arsenic species. The catechol complex used here has been previously shown to undergo the Reimer-Tiemann reaction.(5)

---

(1) J. G. TAIT and M. M. JONES, *J. Amer. Chem. Soc.* **82**, 4196 (1960).

(2) R. L. JETTON and M. M. JONES, *Inorg. Chem.* **1**, 309 (1962).

(3) K. D. MAGUIRE and M. M. JONES, *J. Amer. Chem. Soc.* **84**, 2316 (1962).

(4) J. P. COLLMAN in *Reactions of Co-ordinated Ligands and Homogeneous Catalysis* (Edited by D. H. BUSCH) p. 94. Amer. Chem. Soc., Washington, D.C. (1963).

(5) H. REIHLEN, R. ILLIG and R. WITTIG, *Ber. Chem. Dtsch. Ges.* **58**, 12 (1925).

EXPERIMENTAL

Preparation of the alkali salts of the complex acids The complex L-Na $[As(catechol)_3]$ H_2O was prepared according to the method given by Weinland and Heinzler(6) using modifications in procedure given by Mann and Watson(7), The complex D-Na $[As(3\text{-methylcatechol})_3]$ 2 H_2O was prepared according to the procedure given earlier (8) The catechol complex had a specific rotation of 460 compared to the literature value of −454 The 3-methylcatechol complex had a specific rotation of only +89° compared to the literature value of +385° However, it was felt that this incomplete resolution would not greatly interfere with the work For the catechol complex, (Found C, 48 64 H, 3 25, As, 17 33 Calc for Na $[As(C_6H_4O_2)_3]$ H_2O C, 47 38, H, 3 09, As 17 42 For the 3-methylcatechol complex Found C, 53 82, H, 5 10, As, 15 52 Calc for $Na[As(C_7H_6O_2)_3]$ 2 H_2O C 52 84 H, 4 86, As, 15 69%

Bromination of the D- and L-sodium salts of the complexes The alkali metal salt (0 05 mole) of the arsenic (V) complex with the 1,2-dihydroxybenzene derivative is dissolved in 150 ml water and the pH held between 9 and 10 by the addition of sodium hydroxide when pH paper showed that the pH had dropped below 9 Liquid bromine (0 15 mole) is added slowly over a 10 min period, with constant stirring, and the temperature is held at 75 The progress of the reaction can be observed by the appearance of a precipitate of the brominated complex The product is light tan and is formed in yields of 25 30 per cent Concentration of the solution by evaporation of the solvent gives larger yields, but makes purification of the product more difficult Found C, 26 76 H, 1 62, As, 9 92 Br, 47 94 Calc for the brominated catechol complex, Na $[As(C_6H_3BrO_2)_2(C_6HBr_2O_3)]$ H_2O C 25 96 H, 0 85, As, 9 00, Br, 47 98% Found C, 23 93, H, 1 59, Br, 45 85, As 7 10 Calc for the brominated 3-methylcatechol complex, $Na[As(C_7H_4Br_2O_2)_3]$ 6 H_2O C, 23 90, H, 2 28, Br, 45 50, As, 7 16%

Characterization of the products of the bromination reactions Sodium sulphite, in three-four fold mole excess, is added to the brominated complex which has been dissolved in 7 9N HCl The mixture is heated gently for 6–8 hr and then extracted with diethyl ether Two compounds were extracted from the ether extract when the initial ligand was catechol Sublimation of the extract gives a compound with melting point 86 , which compared to the 87 melting point of 4-bromocatechol Infrared spectra and qualitative analysis according to the procedures given in Beilstein(9) confirm that the compound is 4-bromocatechol A tar-like residue remains after sublimation Successive recrystallizations of the ether extract gave a compound which is probably 3,4,5-tribromocatechol The product softens slightly at temperatures 90–95 , probably due to remaining 4-bromocatechol or oxidation products, and then has a broad melting-point of 134–38° The literature value(10) for 3,4,5-tribromocatechol is 137–38 Found C, 18 69, H, 0 64 Br, 71 05 Calc for $C_6H_3Br_3O_2$ C, 20 55, H, 0 86, Br, 69 10% It would appear that the sample contained small quantities of a more highly brominated product

Similar decomposition of the brominated complex of 3-methylcatechol with arsenic (V) gave a reddish-brown product which was found impossible to crystallize satisfactorily The acetate prepared from this product melted at 136 , compared to the literature value(11) of 138 for the acetate of 3-methyl 4,5-dibromocatechol No other compound could be isolated from the ether extract when the initial ligand was 3-methylcatechol

Diazo-coupling of the alkali salts of the complex acids Concentrated hydrochloric acid (50 ml) was added to *o*-anisidine (0 18 mole) in 50 ml water The temperature was reduced to 5 in a salt ice bath A concentrated aqueous solution of sodium nitrate is added slowly until a slight excess is present as shown by the formation of a blue colour on starch potassium iodide paper The excess sodium nitrate is decomposed by the addition of a small amount of urea The solution is then added to a solution of the alkali metal salt (0 06 mole) dissolved in the 150 ml water which has been cooled in a salt ice bath The pH of the solution is maintained at 9–10 as in the bromination reactions The diazotized *o*-anisidine is added as rapidly as possible, although the temperature of the reaction mixture

(6) R F Weinland and J Heinzler, *Ber Chem Dtsch Ges* **52,** 1316 (1919)

(7) F G Mann and J Watson, *J Chem Soc* 505 (1947)

(8) T H Larkins, Jr and M M Jones, *Inorg Chem* **2,** 142 (1963)

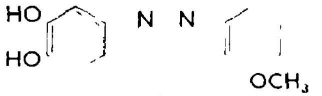
(9) Beilstein, *Handbuch Der Organischen Chemie*, Band 6, p 784 Springer, Berlin (1923)

(10) Beilstein, *Handbuch der Organischen Chemie* Band 6, p 785 Springer, Berlin (1923)

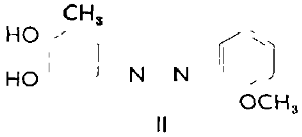
(11) T Zincke and N W Janney, *Ann Chem*, **389,** 351 (1913)

must not be allowed to rise above 5°C. The diazo-coupled complex precipitates and is filtered immediately. The yields are usually rather high, in the neighbourhood of 75 per cent. The products are light reddish-brown. Details of the optical rotation changes of the reactions are given in Table 1. Found: C, 45.65, H, 3.85, N, 5.94, As 11.25. Calc. for the catechol complex $Na[As(C_6H_4O_2)_2(C_{13}H_{12}N_2O_3)] \cdot 5H_2O$: C, 45.32, H, 4.22, N, 4.23, As, 11.31%. Found: C, 52.11, H, 4.52, N, 5.13, As, 11.25. Calc. for the 3-methylcatechol complex, $Na[As(C_7H_6O_2)_2(C_{14}H_{14}N_2O_3)] \cdot H_2O$: C, 54.50, H, 4.25, N, 4.50, As 12.12. It appears that a mixed product was formed which was predominantly the compound shown.

Characterization of the products of the diazo-coupling reactions. The complexes were decomposed in a manner similar to that used for the brominated complexes. For both compounds studied, there were at least two products formed, one soluble and the other insoluble in water. The insoluble product was filtered from the solution before ether extraction. The soluble product was removed by ether extraction. Sublimation of the ether extract gave a product identified by melting point and infra-red spectra as catechol and 3-methylcatechol respectively. The insoluble product in both cases would not form good crystals and characterization of this product was carried out using qualitative organic techniques and infra-red spectra. In both cases a sodium fusion gave a positive test for nitrogen. Infra-red spectra data were consistent with that would be expected for the compounds 2'-methoxy-3, 4-dihydroxy-azobenzene (I) and 2'-methoxy-3, 4-dihydroxy, 5-methylazobenzene (II).



I



II

The spectrum of (I) contained a band at 912 cm^{-1} which has been assigned to a 1, 2, 4-tri-substituted aromatic ring, while the spectrum of (II) contained a band at 850 cm^{-1} assigned to 1, 2, 3, 5-tetra-substitution of the aromatic ring. Compound (I) has been reported in the literature(12) with a melting point of 149° and reddish-brown crystals. We were unable to obtain the compound in other than a very viscous, tar-like form. Compound (II) has not been reported previously.

DISCUSSION

The experimental results show that both diazo-coupling and bromination of the optically active complexes can be achieved without appreciable change of optical activity and presumably configuration (Table 1). This indicates that such reactions must take place with the complex as a whole rather than momentarily disengaged ligand molecules.* The behaviour of the complex during the bromination in basic solution shows that coordination results in an appreciable masking of the phenols towards oxidation, as these are normally very susceptible to attack by such strongly oxidizing media. It is to be noted that the positions of the ligand molecule which are susceptible to attack by electrophilic reagents are not changed by co-ordination, even though the central atom of the complex is in a very high oxidation state. The role played by steric factors in the reactions studied here, especially the diazocoupling, are difficult to evaluate and may be more important than the authors are presently willing to admit.

There is a very general tendency to suspect that coordination exerts profound changes on the reactivity of organic ligands While the evidence on this point is rarely of a comparative nature, it must be emphasized that such evidence as is available indicates that the cordination act per se *need not* result in reaction patterns which are qualitatively different from those of the free ligand [14] In organic chemistry, the common inorganic Lewis acids are used for two chief purposes (1) to form a coordination complex with a substrate and (2) to activate a substrate through the formation of a charge transfer complex These processed are actually distinct, though in many cases they may be concurrent The second of these processes may exert a more profound effect on aromatic reactivity than the first by virture of the more direct involvement of the aromatic pi-electrons This is especially true in systems where the coordination is to a donor atom external to the aromatic system Non-alternant aromatic systems such as tropolone must be expected from this statement [15]

---

* The rates of the dissociation reactions have been measured and found to be much slower than the rates of bromination or diazo-coupling.(13)

(12) V. Kuznetsov and A. Nemodruck, *Sborn. Stat. Obsh. Khim.* **2**, 1378 (1953), *Chem. Abstr.* **48**, 10347g.

(13) T. H. Larkins, Jr., and M. M. Jones, *Inorg. Chem.* **2**, 554 (1963).

TABLE 1 – OPTICAL ROTATION DATA FOR THE BROMINATION AND DIAZO-COUPLING OF THE CATECHOL AND 3-METHYLCATECHOL COMPLEXES OF ARSENIC (V)

	$[\alpha]^{25}_{D}$	$[\alpha]^{25}_{D}$	$[\alpha]^{25}_{D}$
Ligand	Sodium salt	Brominated sodium salt	Diazo-coupled sodium salt
Catechol	−460°	−390°	−502°*
3-methylcatechol	+89°	+117°*	123°*

* Rotation observed in acetone solution All other rotations observed in aqueous solution

An important point, difficult to evaluate at present because of the paucity of data, is the effect of charge of the central species on the reactivity patterns of the ligands In a very general way it may be claimed that the reactions of uncharged complexes, especially if they involve groups which escape the masking effect of co-ordination, are qualitatively similar to those of the free ligand [3] The *rates* of the reaction for the free and co-ordinated ligand may be expected to be greatly different [16] The closer the reactive portion of the ligand is to the central ion, the greater the possibilities for qualitative differences in reactivity The "closeness" may be considered to include groups at the end of a conjugated system which has the central metal atom at the other end

Acknowledgement –We wish to express our thanks to the U S Army Research Office Durham, for financial support of this work

[14] The literature is collected in M M JONES, *Advances in Chemistry Series*, *No* 37, 116–123 (1963)

[15] J W COOK, A R M GIBB and R A RAPHAEL, *J Chem Soc*, 2244 (1951)

[16] K D MAGUIRE and M M JONES, *J Amer Chem Soc* **85**, 164 (1963)

J Inorg Nucl Chem 1963, Vol 25 pp 1491 to 1494 Pergamon Press Ltd Printed in Northern Ireland

THE EFFECT OF TEMPERATURE ON THE SIZE OF SMALL MOLECULES APPLICATIONS TO SOME COBALT (II) COMPLEXES

I D PEAT, P J PROLL and L H SUTCLIFFE
Donnan Chemical Laboratories, The University, Liverpool

(*Received* 23 *May* 1963)

Abstract—An expression has been derived for the dependence on temperature of the radius of a system of quantized harmonic vibrators In applying this to $Co(OAc)_4^{2-}$ and $Co(OAc)_2\,4HOAc$ a spherical model was adopted

RECENTLY, in an investigation of the species of cobaltous acetate in acetic acid,[1] varying the dielectric constant was found to have marked effects on the following equilibria

$$Co(OAc)_2 \overset{k_1}{\rightleftharpoons} Co\,OAc^+ + OAc^-$$

$$Co(OAc)_3^- + OAc^- \overset{k_3}{\rightleftharpoons} Co(OAc)_4^{2-}$$

The configurations of the species $Co(OAc)_2$ and $Co(OAc)_4^{2-}$ are octahedral and tetrahedral respectively, the molecules of solvation being omitted for simplicity By studying the effect of the dielectric constant on each of the equilibria, the radii of $Co(OAc)_2\,4HOAc$ and $Co(OAc)_4^{2-}$ were calculated[1] by means of the relationship[2]

$$\ln K^{-1} = C - \frac{e^2 Z_A Z_B}{kTDr} \tag{1}$$

where C is a constant, K is the equilibrium constant, k is the Boltzmann constant, T is the absolute temperature, Z_A and Z_B are the charges on the ions, D is the dielectric constant, e is the electronic charge and r is the radius of the transition state which is assumed to be approximately that of the united ions Since no preferential co-ordination effects could be traced on the addition of water to these systems it was concluded that the interpretation of the effects as being due to a change in macroscopic dielectric constant is quite valid Confirmation is obtained from the fact that the plots[1] of $\ln K_1^{-1}$ and $\ln \varepsilon_4 K_2 K_3 K_A$ against the inverse of the dielectric constant are linear over a range of dielectric constant of about 6–60 ε_4 is the molar extinction coefficient of $Co(OAc)_4^{2-}$ while K_A is the dissociation constant of sodium acetate and K_2 is the formation constant of $Co(OAc)_3^-$ in the paper cited in reference (1) all these constants are shown to be unimportant in the present discussion

Experimental values of the radius were obtained from a series of measurements for dielectric constants ranging from 6 to 78 at several temperatures between the limits 25 and 64°C The data is listed in Tables 1 and 2 of reference (1) Values of the dielectric constant at different temperatures were calculated from the data of SMYTH and ROGERS[3] for acetic acid and from those of LANGE and ROBINSON[4] for water Fig 1 shows the dependence of the radii of the two cobalt (II) species on temperature An expression may be easily derived for this temperature dependence by assuming the cobalt species to be harmonic vibrators in thermal equilibrium with each other Consider a collection of N molecules, having spherical symmetry, which are in equilibrium at the temperature T They are assumed to behave as harmonic vibrators having only breathing modes with fundamental frequency $\nu^2 = k/4\pi^2\mu$ where k is the bond stretching constant of the molecule and μ its reduced mass Each of the molecules labelled by the quantum number n will possess the energy $E = (n + \frac{1}{2})h$ and may be described by the wave function

---

[1] P J PROLL, L H SUTCLIFFE and J WALKLEY, *J Phys Chem* 65, 455 (1961)

[2] S GLASSTONE, K J LAIDLER and H EYRING, *The Theory of Rate Processes* (1st Ed)p 430 McGraw-Hill, New York (1930)

2

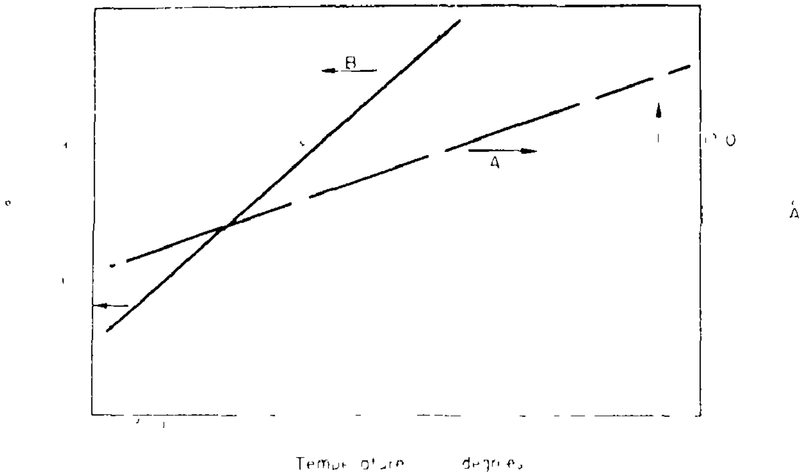


FIG 1 The effect of temperature on the radius of solvated $Co(OAc)_2$ (curve A) and the radius of $Co(OAc)_4^{2-}$ (curve B) ○ are the experimental points r and x the calculated points (RT)

$$\Psi_n(q) = C_n H_n(\gamma^{\frac{1}{2}} q) \exp(-\gamma q^2) \tag{2}$$

where γ is a constant of the motion and given by $\gamma = 4\pi^2\nu/h$, $H_n(\gamma^{\frac{1}{2}}q)$ is the Hermite Polynomial of order n, q is the displacement coordinate and C_n is a normalizing constant

The mean square displacement associated with the wave function $\psi_n(q)$ is given by

$$\overline{D^2}(n) = \langle\psi_n(q)\,|q^2|\,\psi_n(q)\rangle = \frac{n + \frac{1}{2}}{\gamma} \tag{3}$$

and thus the number average displacement for the collection is

$$\overline{D^2}(T) = \frac{\sum_{n=0}^{r} N_n(T)\overline{D^2}(n)}{\sum_{n=0}^{r} N_n(T)} \tag{4}$$

---

[3] C P SMYTH and H E ROGERS, *J Amer Chem Soc* **52**, 1824 (1930)

[4] E LANGE and A L ROBINSON, *J Amer Chem Soc* **52**, 2811 (1930)

when $N_n(T)$ is given by the Boltzmann Law $N_n(T) = N \exp[-(n+\frac{1}{2})h\nu/kT]$. The expression for $\overline{D^2}(T)$ may be reduced to

$$\overline{D^2}(T) = \frac{1}{2\gamma}\left[1 + \frac{2\exp(-2h\nu/kT)}{1 - 2\exp(-h\nu/kT)}\right] \tag{5}$$

and an average value for the radius of the molecules in the collection defined as

$$R(T) = R(O) + [\overline{D^2}(T)]^{\frac{1}{2}} \tag{6}$$

where $R(T)$ represents the mean radius at any temperature T, while $R(O)$ is the mean radius at absolute zero.

Real molecules have degrees of symmetry lower than spherical, however due to their random motion and rotations the view presented to a given molecule in the course of many collisions is one of vibrating spheres and thus Equation (6) may be applied. In the case of polyatomic molecules several vibrational modes may occur and thus summation in (4) must be made over the terms $\overline{D^2}(n, i)$ when

$$\overline{D^2}(n, i) = \langle\psi_n(q_i)\,|q_i^2|\,\psi_n(q_i)\rangle$$

q_i being the normal displacement coordinate of the "ith" vibrational mode.

The general members of the sum $\overline{D^2}(n, i)$ are smaller than the terms representing the displacements of the breathing mode. Thus the numerical value of $\overline{D^2}(T)$ will be smaller in the case of real molecules than that calculated for simple "spherical" molecules. However, for ligands whose masses are small compared with the mass of the central atom, the effect is small, calculation of the magnitude of this effect in the cases of the tetrahedron and the octahedron discussed below gave values less than the experimental errors involved.

The variation of radius with temperature which is given by expression (6) is similar to that found experimentally for the cobaltous acetate species in acetic acid.

With γ and ν as variable parameters, the values of $R(T)$ obtained by Equation (6) were fitted to the experimental results, using a method of least squares, these results are given in Fig. 1. In both cases a value of 200 cm^{-1} for the fundamental frequency of vibration was required. For solvated $Co(OAc)_2$ the calculated curve was made to fit that obtained experimentally by using the value of 2.0×10^{-8} cm for $(2\gamma)^{-\frac{1}{2}}$, in the case of $Co(OAc)_4^{2-}$ a value of 5.0×10^{-8} cm was needed.

The frequency of 200 cm^{-1} obtained is in good agreement with the experimental vibration frequency of 248 cm^{-1} found for $Co(H_2O)_6^{2+}$ from the near infra-red spectra of dilute aqueous solutions of cobaltous halides(5). The observed frequency is a totally symmetric A_{1g} type vibration(6) as required for comparison with our model of a spherical aggregate. Octahedral ammines and hydrates of the divalent states of the first row transition metal series have symmetric vibration frequencies[5,6] in the range 250–400 cm^{-1}.

The radii calculated from expression (1) are probably too large (of the order of 10–20 Å), but it should be remembered that, in water 2:1 electrolytes have Bjerrum radii of about 7 Å The change in radii with temperature appears to fit the calculated values quite reasonably for the bond vibrations invoked If calculations of radius variations over wider temperature ranges were proposed then expression (5) would have to be modified to include anharmonic vibration terms and vibration modes whose degree of symmetry is less than that of the "breathing mode"

---

(5) M. L. Schultz, *J. Chem. Phys.* **10**, 194 (1942).

(6) S. Koide and M. H. L. Pryce, *Phil. Mag.* 3, 607 (1958).

Acknowledgement—The authors are indebted to Drs J H BINKS and T B GRIMLEY for helpful discussion

J. Inorg. Nucl. Chem. 1963, Vol. 25, pp. 1495 to 1502. Pergamon Press Ltd. Printed in Northern Ireland

THE THERMAL DECOMPOSITION OF METAL COMPLEXES—VIII

SOME DIAQUOTETRAMMINECOBALT (III) AND HALOAQUOTETRAMMINECOBALT (III) HALIDES[1]

W. W. Wendlandt, W. R. Robinson and W. Y. Yang
Department of Chemistry, Texas Technological College, Lubbock, Texas

(*Received* 1 *April* 1963)

Abstract—The thermal dissociation of $[Co(NH_3)_4(H_2O)_2]X_3$ and $[Co(NH_3)_4(H_2O)X]X_2$ (X = Cl, Br) was studied by thermo-gravimetric analysis, differential thermal analysis, gas evolution analysis and reflectance spectroscopy. The diaquo-complexes deaquated stepwise $[Co(NH_3)_4(H_2O)_2]X_3 \xrightarrow{I} [Co(NH_3)_4(H_2O)X]X_2 \xrightarrow{II} [Co(NH_3)_4X_2]X$, the final product then dissociated to give CoX_2, N_2, NH_4X and NH_3. The kinetics of the deaquation for step I was determined and found to be first order with E^* equal to 33 and 21 kcal, for the chloride and bromide complexes, respectively.

Jorgensen[2] was the first to observe that the diaquotetramminecobalt (III) halides were thermally unstable in the solid state. He found, in a qualitative manner, that the complexes deaquated stepwise according to the reactions: ($X^- = Cl$ and Br)

$$[Co(NH_3)_4(H_2O)_2]X_3 \xrightarrow{I} [Co(NH_3)_4(H_2O)X]X_2 + H_2O \xrightarrow{II} [Co(NH_3)_4X_2]X + H_2O$$

Both reactions proceeded slowly at ambient temperature but increased in rate rapidly at 100° and 150° for steps (I) and (II), respectively. Later studies by Mori *et al.*[3] confirmed these deaquations reactions but that the deaquation temperatures were somewhat lower. Reaction I took place from 70° to 90° and II from 150° to 170°. It was also stated that the dichloro-complex began to decompose at about 240°.

In connection with our previous studies on the aquopentamminecobalt (III),[4] aquopentamminechromium (III),[5] and hydroxoaquotetramminecobalt (III)[6] complexes, it was of interest to study the thermal dissociation of the diaquotetramminecobalt (III) halide complexes by the methods of thermogravimetry (TGA), differential thermal analysis (DTA), gas evolution analysis (GE), and reflectance spectroscopy.

EXPERIMENTAL

Preparation of complexes. The $[Co(NH_3)_4(H_2O)_2]X_3$ and $[Co(NH_3)_4(H_2O)X]X_2$ complexes were prepared as previously described.[2] The cobalt contents of these compounds were determined by ignition of the complexes, mixed with oxalic acid, in a porcelain crucible to 800° and weighing as Co_3O_4. The water contents were determined by weight-loss on a thermobalance. The results of the analyses were: $[Co(NH_3)_4(H_2O)_2]Cl_3$: Co, 21.9% found, 21.87% theor.; H_2O, 13.5% found, 13.38% theor.; $[Co(NH_3)Cl(H_2O)]Cl_2$: Co, 23.5% found 23.44% theor.; H_2O, 7.0% found, 7.17% theor. $[Co(NH_3)_4(H_2O)_2]Br_3$: Co, 14.8% found, 14.63% theor.; H_2O, 8.7% found, 8.95% theor.; $[Co(NH_3)_4Br(H_2O)]Br_2$: Co, 15.4% found, 15.32% theor.; H_2O, 4.0% found 4.68% theor.

---

[1] For Part (VII) see W. W. Wendlandt and J. P. Smith, *J. Inorg. Nucl. Chem.* **25**, 1267 (1963).

[2] S. M. Jorgensen, *Z. Anorg. Chem.* **2**, 294 (1892).

[3] M. Mori, R. Tsuchiya, S. Takemura and E. Matsuda, *Bull. Chem. Soc. Japan* **34**, 1757 (1961).

[4] W. W. Wendlandt and J. L. Bear, *J. Phys. Chem.* **65**, 1516 (1961).

[5] W. W. Wendlandt and J. J. Bear, *J. Inorg. Nucl. Chem.* **22**, 77 (1962).

[6] W. W. Wendlandt and J. K. Fisher, *J. Inorg. Nucl. Chem.* **24**, 1685 (1962).

Thermobalance, air atmosphere The automatic recording thermobalance has previously been described(7) Sample sizes weighed about 100 mg and were pyrolysed in a static air atmosphere at a furnace heating rate of 6–7 C per min

Thermobalance, nitrogen atmosphere The automatic recording thermobalance has previously been described (8) Sample sizes ranged in weight from 20 to 50 mg After evacuation of the balance it was filled with dry nitrogen gas which was then passed over the sample container at a rate of about 100 ml per min The furnace heating rate was about 5°C per min

Differential thermal analysis-gas evolution apparatus This apparatus has previously been described (9) Sample sizes ranged in weight from 40 to 60 mg and were pyrolysed in a dynamic helium atmosphere The furnace heating rate was about 10 C per min

Vacuum pyrolysis studies Samples of the complexes were pyrolysed in a tube furnace connected to a high vacuum system Provision was made for the collection of the decomposition gases in a 126 ml glass bulb which could be removed from the system by means of a ground-glass joint About 100 mg of sample was pyrolysed to temperatures up to 600 The composition of the decomposition gases was determined by a mass spectrometer

Reflectance studies The high temperature reflectance curves were obtained on a Bausch and Lomb Spectronic 505 spectrophotometer using a heated sample holder (10) The freshly prepared samples were examined at a sample heating rate of 6–7 per min A chromel-alumel thermocouple imbedded in the sample, was used to monitor the sample temperature The wavelength range was from 350 to 750 mμ

RESULTS AND DISCUSSION

Weight-loss studies in air The weight-loss curves of the complexes, in air, are given in Fig 1

The weight-loss curve for $[Co(NH_3)_4(H_2O)_2]Cl_3$ showed that deaquation began at 75°–80° and resulted in a break in the curve at 100° which corresponded to the stoicheiometry, $[Co(NH_3)_4(H_2O)Cl]Cl_2$ Further weight-loss then took place, resulting in another break in the curve which at 160° corresponded closely to the composition, $[Co(NH_3)_4Cl_2]Cl$ Another curve break was observed at about 300° but no known composition could be assigned to it The curve break at 390° corresponded closely to that for $CoCl_2$ Since the pyrolysis was carried out in air, the residue Co_3O_4, was obtained at about 900° It should be pointed out that definite horizontal weight levels were not obtained in the curves Thus, the composition of the intermediate complexes may be fortuitous although the weight-losses indicated the above stoicheiometries

The weight-loss curve for $[Co(NH_3)_4(H_2O)Cl]Cl_2$ was similar to that for the diaquo-complex, after the loss of the first mole of water The first weight-loss began at about 120° A break in the curve was obtained at about 200° which corresponded to the composition, $[Co(NH_3)_4Cl_2]Cl$ The remainder of the curve was similar to the diaquo-complex except that the Co_3O_4 weight-level was obtained at a lower temperature than in the former case

The weight-loss curve for $[Co(NH_3)_4(H_2O)_2]Br_3$ showed that deaquation began at 85°–90°, giving a break in the curve at 110° which corresponded to the composition $[Co(NH_3)_4(H_2O)Br]Br_2$ Another break in the curve was observed at 170° which approached the composition, $[Co(NH_3)_4Br_2]Br$ Further decomposition at higher temperatures gave a short horizontal weight level from 260 to 300° which corresponded closely to the composition for a 1 1 molar mixture, $CoBr_2 \cdot NH_4Br$

---

(7) W W Wendlandt, T D George and G R Horton, *J Inorg Nucl Chem* **17**, 274 (19

(8) T D George and W W Wendlandt, *J Inorg Nucl Chem* **25**, 395 (1963)

(9) W W Wendlandt, *Analyt Chem Acta* **27**, 309 (1962)

(10) W W Wendlandt, P H Franke and J P Smith, *Analyt Chem* **35**, 105 (1963)

that by a surrounding liquid. Such a conclusion further implies that reaction (1) occurs in a location that has not been greatly disturbed by the arrival of the tritium atom: the reaction does not occur in a molten drop, or the organic equivalent of a displacement spike.

Secondly, the rate of reaction (2) depends upon the total excess energy of the radical both from the excess kinetic energy of the incoming tritium atom and from the initial internal energy of the *trans*-butene-2 molecule. The average internal energy of the target molecule is 0.83, 0.56 and 0.22 eV for 20°C, −78°C and −196°C, respectively. This amount is not negligible relative to the activation energy for reaction (2) of 1.4 ev,[illegible] but the similarity between the liquid runs at different temperatures suggests that this is not the major source of the experimental variations.

Further, while the possibility seems much less likely than with radioactive atoms in inorganic crystals,(8,9,10) consideration must be given to the possibility that some of the reactions involving the tritium atom (or an unstable species containing the tritium) do not occur until the experimental container is allowed to warm up after completion of the irradiation.

Further experiments on several target molecules over a range of temperatures appear to be necessary in order to determine the relative contributions of phase and the other possible sources of the observed variation in tritium activity distribution. It should also be emphasized that the same general mechanisms of reaction seem to be operative in all phases, for the semi-quantitative behaviour of recoil tritium atoms is essentially identical in all of these experiments.

Experimental

The *trans*-butene-2 samples were sealed in capillaries containing approximately an equal weight of LiF and irradiated for one pulse of the GA TRIGA reactor in San Diego. The neutron flux averaged about 6×10^{15} n/cm²/sec over a 15 msec period in these irradiations. Since the delay time between insertion of a sample into position in the reactor and irradiation was only about 30 sec, crude refrigeration techniques were quite satisfactory. The −196°C irradiation was carried out with pre-cooled samples in a TRIGA tube filled with liquid nitrogen. Some of this coolant was still visible with hurried removal of the tube from the reactor after irradiation.

Subsequent to irradiation, the samples were analysed as in previous experiments.[illegible]

Acknowledgment—We wish to thank General Atomics for making their facilities available to us for carrying out these irradiations.

Department of Chemistry
University of Kansas

E. K. C. Lee
F. S. Rowland

(8) S. Veljković and G. Harbottle, *Nature (Lond.)* **191**, 1287 (1961).
(9) S. Veljković and G. Harbottle, *J. Inorg. Nucl. Chem.* **23**, 159 (1961).
(10) W. J. Hoff, Jr. and F. S. Rowland, *J. Inorg. Nucl. Chem.* **5**, 164 (1958).

Sublimation of the NH_4Br and subsequent oxidation of $CoBr_2$ to Co_3O_4 then took place from 325° to 650°

The weight-loss curve for $[Co(NH_3)_4(H_2O)Br]Br_2$ was similar to that found for the diaquo-complex, after the loss of the first mole of water Deaquation began at about 140°, giving a break in the curve at 185° which corresponded to the composition, $[Co(NH_3)_4Br_2]Br$ Further decomposition at higher temperatures gave a curve which was similar to that found for the diaquo-complex

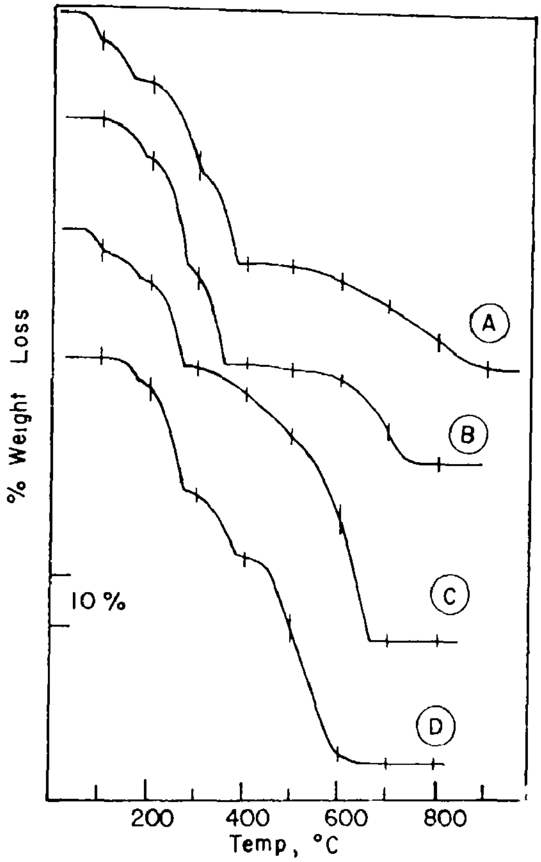


FIG. 1 —Weight-loss curves of cobalt amine complexes Air atmosphere
A $[Co(NH_3)_4(H_2O)_2]Cl_3$ *C* $[Co(NH_3)_4(HO_2)_2]Br_3$
B $[Co(NH_3)_4(H_2O)Cl]Cl_2$ *D* $[Co(NH_3)_4(H_2O)Br]Br_2$

Thus, in air, the dissociation of the complexes follows the pattern previously suggested$^{(2,3)}$ except that the terminal pyrolysis product is the oxide, Co_3O_4

Weight-loss studies in nitrogen, The weight-loss curves of the complexes in a nitrogen atmosphere are given in Fig 2

In general, the same curve breaks were obtained for the complexes in a nitrogen atmosphere as were found in the air atmosphere studies indicating that decomposition reactions and not oxidation reactions were taking place The decomposition temperatures were 5°–10° lower but this may be due to instrumental differences or to the difference in furnace atmospheres i e , dynamic versus static atmosphere, etc

The weight-loss curve for $[Co(NH_3)_4(H_2O)_2]Cl_3$ shows that the deaquation reaction began at about 65° A break in the curve, at 100°, corresponded to the composition for the chloroaquo-complex Another curve break, at 180°, corresponded to the stoicheiometry for the dichloro-complex, $[Co(NH_3)_4Cl_2]Cl$ From 180° to 29 further dissociation took place, giving a break in the curve at 300° which roughly corresponded to the composition for a 1 1 molar mixture of $CoCl_2$ and NH_4Cl Above 300°, the NH_4Cl sublimed off, giving a residue of $CoCl_2$ at about 375°

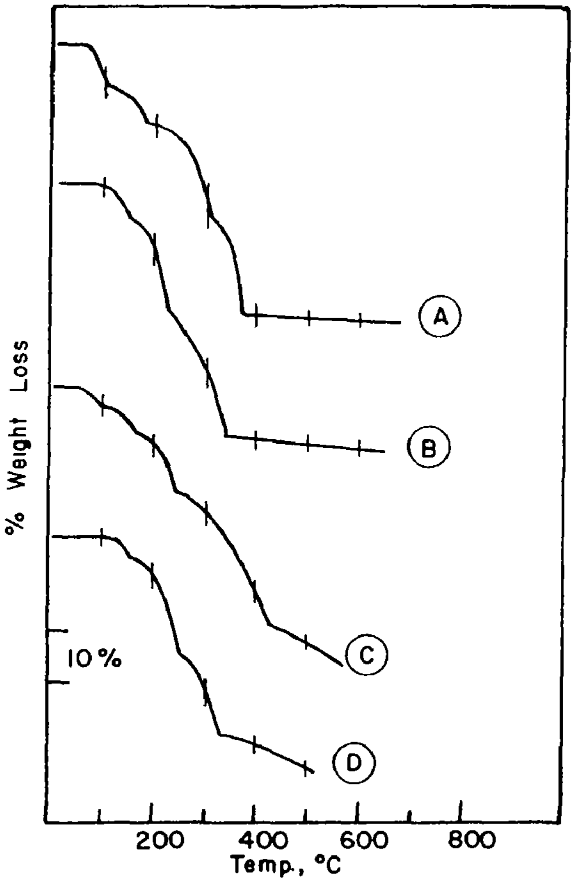


Fig 2 -Weight-loss curves of cobalt amine complexes Nitrogen atmosphere

A $[Co(NH_3)_4(H_2O)_2]Cl_3$ *C* $[Co(NH_3)_4(H_2O)_2]Br_3$
B $[Co(NH_3)_4(H_2O)Cl]Cl_2$ *D* $[Co(NH_3)_4(H_2O)Br]Br_2$

The behaviour of the chloroaquo-complex, $[Co(NH_3)_4(H_2O)Cl]Cl_2$, was similar to that of the diaquo-complex, after the loss of the first mole of water

The weight-loss curve for $[Co(NH_3)_4(H_2O_2]Br_3$ showed that the deaquation reaction began at about 55° Curve breaks, at 100°, 160° and 235°, corresponded to the compositions, $[Co(NH_3)_4(H_2O)Br]Br_2$, $[Co(NH_3)_4Br_2]Br$, and a 1 1 molar mixture of $CoBr_2$ and NH_4Br, respectively The composition of the curve at 420° corresponded to that for $CoBr_2$ Above 425°, the $CoBr_2$ began to sublime

The behavior of the bromoaquo-complex, $[Co(NH_3)_4(H_2O)Br]Br_2$, was similar to that of the diaquo-complex, after the loss of the first mole of water

Differential thermal analysis–gas evolution studies The DTA–GE curves for the complexes are given in Figs 3 and 4

All of the complexes gave a series of endothermic peaks which correspond to the deaquation and decomposition reactions of the compound Only in the case of the diaquo- and chloroaquo-chloride complexes was an exothermic peak obtained in the curve

The DTA curve for $[Co(NH_3)_4(H_2O)_2]Cl_3$ had six endothermic peaks and one exothermic peak The first peak, with a peak maximum temperature (henceforth referred to as peak temperature) at 55°, was due to the evolution of residual ether which was used to wash the complex The peaks at 110 and 180° were due to the deaquation of the first and second moles of water, per mole of complex, respectively The exothermic peak, at 200°, was due to some type of a phase change, isomeric transition, or crystalline structure transition since a GE peak was not observed in this temperature range A possible explanation for this peak is that perhaps *trans*- $[Co(NH_3)_4Cl_2]Cl$ is first formed in the deaquation of $[Co(NH_3)_4(H_2O)Cl]Cl_2$ The isomerization of *trans*- to *cis*- $[Co(NH_3)_4Cl_2]Cl$ could possibly cause the exothermic peak since the *cis*-compound, in agreement with Mori *et al*,(3) was formed during the dissociation reaction The increased thermal stability of $[Co(NH_3)_4(H_2O)Cl]Cl_2$ may possibly be due to the trans-effect which was previously discounted by Mori and co-workers(3) The latter contend that *cis*-$[Co(NH_3)_4Cl_2]Cl$ is more stable than *trans*-$[Co(NH_3)_4Cl_2]Cl$ The remaining peaks, at 260°, 290°, and 350° were due to the decomposition of the dichloro-complex, $[Co(NH_3)_4Cl_2]Cl$ All of them involved gaseous decomposition products as shown by the GE curve

The DTA-GE curves for $[Co(NH_3)_4(H_2O)Cl]Cl_2$ were similar to those found for the diaquo-complex except for the heights of the peaks which was caused by the difference in sample sizes All of the peaks were present except the 55 and 110° endothermic peaks

The DTA curve for $[Co(NH_3)_4(H_2O)_2]Br_3$ consisted of three main endothermic peaks The first two peaks, at 90° and 160° were due to the deaquation reactions for the two moles of water No phase transition was observed for this complex as was found with the diaquo-chloride compound Only one endothermic peak, at 220°, was observed for the dissociation of the dibromo-complex $[Co(NH_3)_4Br_2]Br$ All of the DTA peaks evolved gaseous products

The DTA curve for $[Co(NH_3)_4(H_2O)Br]Br_2$ was similar to that found for the diaquo-complex after the evolution of the first mole of water The peak temperatures were shifted to slightly higher temperatures, however

Vacuum pyrolysis studies Analysis of the gaseous decomposition products formed during the pyrolysis of the complexes *in vacuo*, revealed only the presence of water, ammonia and nitrogen Ammonium halide was deposited on the cool part of the tube furnace while the residue remaining in the furnace chamber was the cobalt halide The water, of course, comes from the deaquation reaction while the other products probably are formed by the reactions

$$[Co(NH_3)_4X_2]X \longrightarrow CoX_2 + NH_4X + N_2 + NH_3$$

This type of dissociation is similar to that previously found in the thermal dissociation of the $[Co(NH_3)_6]X_3$(11) and $[Co(NH_3)_5X]X_2$(12) complexes The co-ordinated ammonia is the reducing agent for the Co(III) → Co(II) reduction

---

(11) W W Wendlandt, *J Inorg Nucl Chem* **25**, 545 (1963)

(12) W W Wendlandt and J P Smith, *J Inorg Nucl Chem* **25**, 843 (1963)

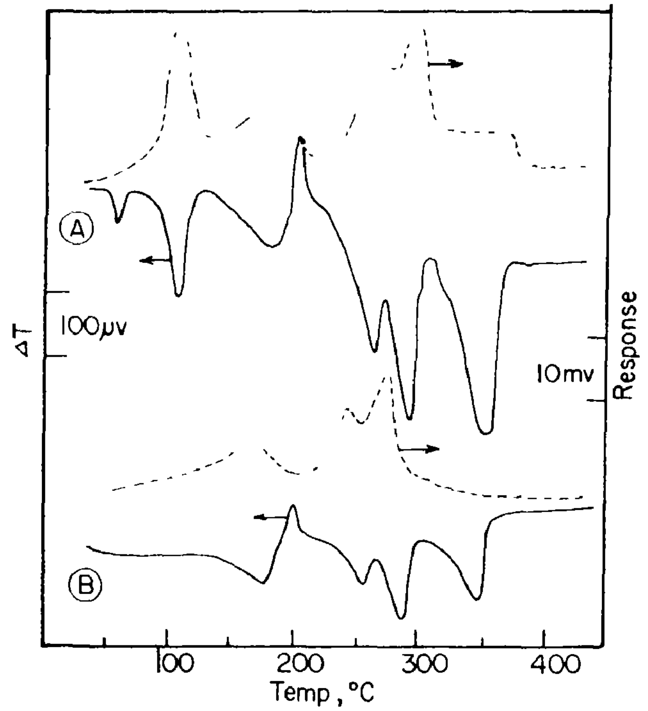


FIG 3—DTA–GE curves of cobalt amine complexes (Dashed lines are GE curves)
A $[Co(NH_3)_4(H_2O)_2]Cl_3$ *B* $[Co(NH_3)_4(H_2O)Cl]Cl_2$

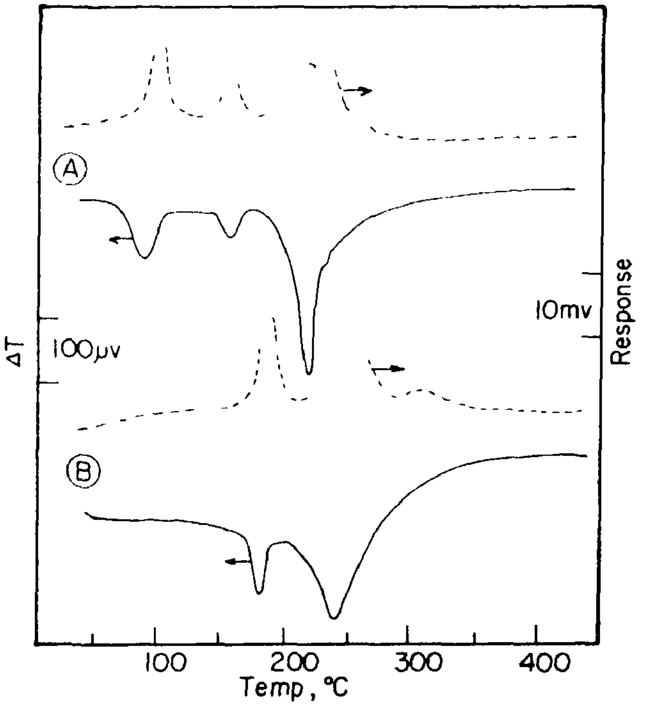


FIG 4—DTA–GE curves of cobalt amine complexes. (Dashed lines are GE curves)
A $[Co(NH_3)_4(H_2O)_2]Br_3$ *B* $[Co(NH_3)_4(H_2O)Br]Br_2$

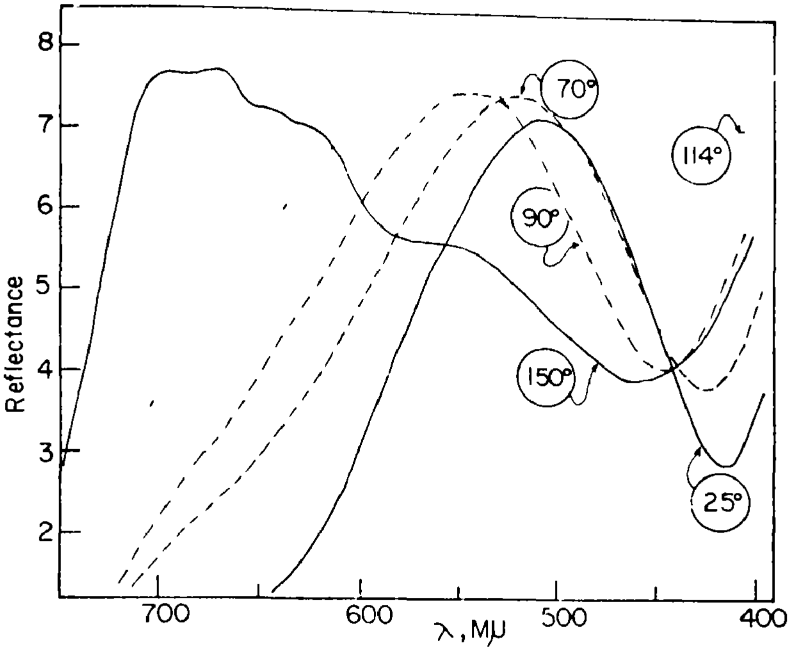


FIG. 5 —High temperature reflectance spectra curves of $[Co(NH_3)_4(H_2O)_2]Cl_3$ Sample surface temperature indicated

Kinetics of deaquation studies Using the non-isothermal thermogravimetric method of FREEMAN and CARROLL,(13) the kinetics of the deaquation reaction, in nitrogen, were determined for three of the complexes For the reaction

$$[Co(NH_3)_4(H_2O)_2]X_3 \xrightarrow{\Delta} [Co(NH_3)_4(H_2O)X]X_2 + H_2O(v)$$

the activation energies, *E**, in kcal, and reaction orders, *n*, were Cl, 33, 1, Br, 21, 1 For the second deaquation reaction

$$[Co(NH_3)_4(H_2O)Cl]Cl_2 \xrightarrow{\Delta} [Co(NH_3)_4Cl_2]Cl \quad H_2O(v)$$

the *E** was 22 kcal and *n* was 1 Results obtained for the corresponding bromide compound were very erratic and did not give a straight line plot The activation energy for the chloroaquo-complex was fairly close to that previously reported for the deaquation of $[Co(NH_3)_5H_2O]Cl_3$(4,14) while that for the first water loss of $[Co(NH_3)_4(H_2O)_2]Br_3$ was close to the value of 25 kcal previously reported for $[Co(NH_3)_5H_2O]Br_3$ (4)

Reflectance studies The high temperature reflectance curves for $[Co(NH_3)_4(H_2O)_2]Cl_3$ and $[Co(NH_3)_4(H_2O)Cl]Cl_2$ are given in Figs 5 and 6, respectively

Due to the wavelength limitation of the instrument only one peak was observed for $[Co(NH_3)_4(H_2O)_2]Cl_3$, at 510 mμ On heating this compound, in a nitrogen atmosphere, the peak maxima shifted to longer wavelengths, due to the formation of the aquochloro-complex, $[Co(NH_3)_4(H_2O)Cl]Cl_2$ At still higher temperatures, the single peak disappeared, giving the curve for the dichlorotetrammine-complex Thus, the deaquation reaction can be followed by the reflectance spectra at elevated temperatures

(13) E S FREEMAN and B CARROLL *J Phys Chem* **62**, 394 (1958)

(14) M MORI, R TSUCHIYA and Y OKANO, *Bull Chem Soc Japan* **32**, 1029 (1959)

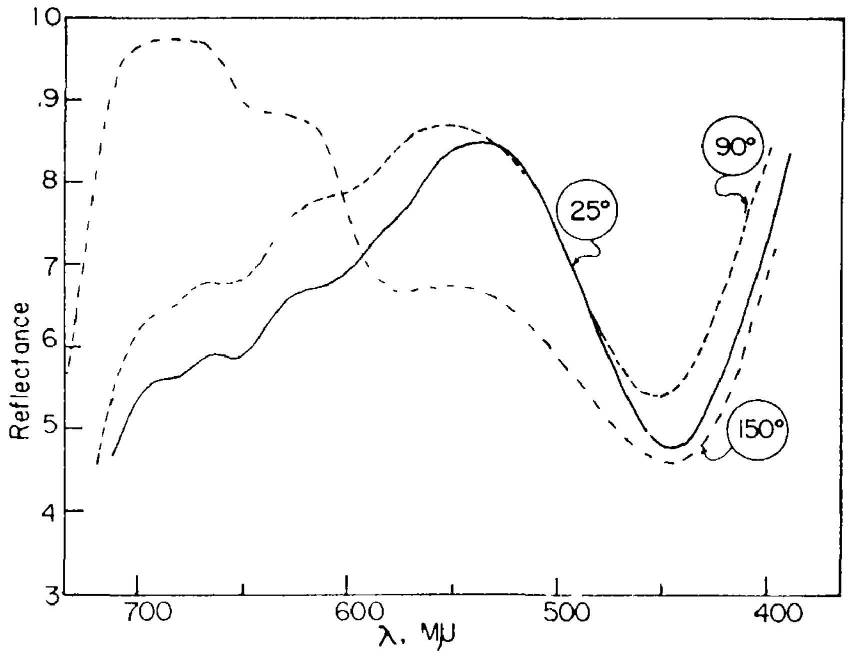


FIG. 6.—High temperature reflectance spectra curves of $[Co(NH_3)_4(H_2O)Cl]Cl_2$. Sample surface temperature indicated.

The reflectance curve for $[Co(NH_3)_4(H_2O)Cl]Cl_2$, at room temperature, has a peak maximum at about 540 mμ with some indication of peak maximas in the 600–700 mμ range. On heating, the 540 mμ shifts to longer wavelengths, then disappears to give the curve for $[Co(NH_3)_4Cl_2]Cl$. This was similar to that found for the diaquo-complex.

General. From the above, it is seen that the diaquo-complexes deaquate in a stepwise manner to give the dihalotetramminecobalt (III) compounds. If the minimum weight-loss temperatures are taken as an approximate criteria for the thermal stability of the complexes, the order is clearly: chloride > bromide complexes. This is the same order as was found for the $[Co(NH_3)_5H_2O]X_3$ type complexes.(4) Likewise, the decomposition of the dihalotetramminecobalt (III) complexes was similar to that previously reported for the hexammine- and pentamminecobalt-(III) complexes.

Acknowledgement—The support of this work by the Robert A. Welch Foundation of Houston, Texas, is gratefully acknowledged.

J Inorg Nucl Chem 1963, Vol 25 pp 1503 to 1506 Pergamon Press Ltd Printed in Northern Ireland

FORMATION OF DIBORANE BY THE INTERACTION OF DISILANE WITH BORON TRICHLORIDE*

C H VAN DYKE† and A G MACDIARMID‡

John Harrison Laboratory of Chemistry, University of Pennsylvania, Philadelphia

(*Received* 16 *March* 1963, *in revised form* 7 *May* 1963)

Abstract Although BCl_3 does not react with SiH_4, it does react with Si_2H_6 at 0 to give quantitative yields of B_2H_6 and polychlorodisilanes No reaction occurs between SiH_3Cl and BCl_3, or between BI_3 and Si_2H_6 A possible reaction mechanism is proposed

As part of a continuing study of the properties of the silicon-silicon bond,(1-3) it was considered desirable to determine whether disilane would react with BCl_3 The investigation was prompted by the fact that the higher silanes have been reported to react readily with several halogenated compounds such as $CHCl_3$,(4) and PI_3,(5) etc , under mild conditions Since no reactions of this type have been reported to occur with SiH_4, it appears that the reactions are in some way related to the presence of a silicon–silicon bond in the molecule

RESULTS AND DISCUSSION

STOCK and STIEBELER(4) found that reaction occurred with explosive violence between Si_2H_6, Si_3H_8 or Si_4H_{10} and CCl_4 or $CHCl_3$ when even a trace of dissolved air or oxygen was present However, with pure $CHCl_3$ and Si_3H_8, a controllable reaction took place at 50–70° in the presence of Al_2Cl_6 catalyst to give CH_4, CH_3Cl, CH_2Cl_2, and polychlorotrisilanes of the type $Si_3H_4Cl_4$, etc No reaction occurred when SiH_4 was used in place of the higher silanes In analogous types of reactions, EMELÉUS and MADDOCK(5) have reported that Si_4H_{10} underwent reaction slowly with CHI_3 at room temperature and rapidly with PI_3 at 100 without catalyst, to give presumably iodotetrasilanes, whereas with substances such as $CHCl_3$ and $CHBr_3$, Al_2Cl_6 catalyst was necessary In the latter reactions, the corresponding methylene halides were obtained in addition to halogenated polysilanes

SCHAEFFER and ROSS(6) have reported that SiH_4 underwent reaction with BCl_3 to give a 67 per cent yield of B_2H_6 when it was mixed with CH_3NNCH_3 and irradiated with ultra-violet light. The photo-decomposition of the CH_3NNCH_3 produced fr radicals which were presumed to initiate the reaction. However, it was not clear whether it had definitely been proven that SiH_4 and BCl_3 did not react in the absence of CH_3NNCH_3.

---

* This report is based on portions of a thesis to be submitted by C H VAN DYKE to the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy This study is in part a contribution from the Laboratory for Research on the Structure of Matter, University of Pennsylvania, supported by the Advanced Research Projects Agency, Office of the Secretary of Defense

† DuPont Teaching Fellow.

‡ Alfred P Sloan Fellow

(1) L G L WARD and A G MACDIARMID, *J Inorg Nucl Chem* **21**, 287 (1961)
(2) A D CRAIG, J V URENOVITCH and A G MACDIARMID, *J Chem Soc* 548 (1962)
(3) J V URENOVITCH and A G MACDIARMID, *J Chem Soc* 1091 (1963)
(4) A STOCK and P STIEBELER, *Ber Dtsch Chem Ges* 56B, 1087 (1923)
(5) H J EMELÉUS and A G MADDOCK *J Chem Soc* 1131 (1946)
(6) R SCHAEFFER and L ROSS, *J Amer Chem Soc* **81**, 3486 (1959)

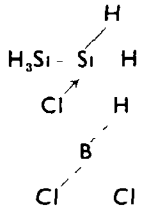
It was determined in this investigation that SiH_4 or the substituted silane, SiH_3Cl, underwent no reaction whatsoever with BCl_3 in the vapour phase at 0° during a period of 12.5 hr. Under identical experimental conditions, Si_2H_6 and BCl_3 in the molar ratio of approximately 2 : 1 were found to react to give 100% yields of B_2H_6 and a mixture of Si_2H_5Cl, $Si_2H_4Cl_2$ and $Si_2H_3Cl_3$. When the molar ratio of Si_2H_6 to BCl_3 was increased to 9 : 1, no $Si_2H_3Cl_3$ was formed, but some $Si_2H_4Cl_2$ was produced in addition to Si_2H_5Cl. Infrared evidence suggested that when the above reaction was carried out at low temperatures, intermediate species, possibly chlorodiboranes, were formed which decomposed to give B_2H_6. This appears likely since chlorodiboranes are reported to decompose rapidly.[7] The first two steps in the reaction would therefore appear to be as follows:

$$Si_2H_6 + BCl_3 \rightarrow Si_2H_5Cl + \tfrac{1}{2}(HBCl_2)_2$$
$$3(HBCl_2)_2 \rightarrow B_2H_6 + 4BCl_3.$$

Further chlorination of the Si_2H_5Cl could then occur to give the polychlorodisilanes.

It was particularly interesting to find that BF_3 underwent no reaction whatsoever with Si_2H_6 even after 19 hr at room temperature. This difference in behaviour with BF_3 is probably not due to thermodynamic factors since the difference in bond energy between B—Cl and Si—Cl is 18 kcal/mole and that between B—F and Si—F is 19 kcal/mole, the boron–halogen bond having the greater bond energy in each case.[8] Entropy factors would be expected to be similar in analogous reactions involving BCl_3 and BF_3.

Reaction may proceed by a rate-determining step involving electrophilic attack of a hydrogen by BCl_3, or by nucleophilic attack of the silicon by chlorine. In either case the BCl_3 might be expected to react more rapidly. Since BF_3 is a weaker Lewis acid than BCl_3,[9] the formation of a Si · H · B bridge would be less likely to occur with BF_3. The tendency for nucleophilic attack of the silicon by a halogen is also likely to be less with BF_3. In this case, the electron density on the fluorine atoms will be reduced considerably because of $p_\pi - p_\pi$ interaction between the fluorine and the boron, which is greater than that between chlorine and boron in BCl_3.[10] In either case, a four center transition state such as (A) could be involved.



(A)

---

[7] H. I. SCHLESINGER and A. B. BURG, *J. Amer. Chem. Soc.* **53**, 4321 (1931); A. STOCK, F. K and O. PRIESS, *Ber. Dtsch. Chem. Ges.* **47**, 3115 (1914).

[8] T. L. COTTRELL, *The Strengths of Chemical Bonds*, Butterworths, London (1958).

[9] H. C. BROWN and R. R. HOLMES, *J. Amer. Chem. Soc.* **78**, 2173 (1956).

[10] L. PAULING, *The Nature of the Chemical Bond*, 3rd Ed., p. 318. Cornell, Ithaca, New York (1960).

The observation that Si_2H_6, but not SiH_4 or SiH_3Cl, reacts with BCl_3 is consistent with the greater reactivity generally noted for compounds containing a silicon-silicon bond(2,11 12) For example, Si_2H_5I and $(Si_2H_5)_2O$ are spontaneously inflammable in air, whereas SiH_3I and $(SiH_3)_2O$ are not(11) It has been suggested previously that attack of a silicon atom at a silicon-silicon bond may proceed through the simultaneous overlap of a *d*-orbital on each silicon, by a filled *p*-orbital of the attacking group(2) This would give a transition state analogous to a structure proposed for $Al_2(CH_3)_6$ in which an SP^3 orbital of a bridge methyl overlaps an SP^3 orbital of each aluminium atom simultaneously(13) If the silicon-silicon bond in Si_2H_6 should undergo attack of this type by a chlorine of BCl_3, then the charge would be distributed over two silicon atoms rather than one, thus promoting formation of the transition state A somewhat similar explanation has been offered to explain the fact that Si_2H_6 reacts more rapidly than SiH_4 with HI(11)

It is of interest to note that BCl_3, in addition to not reacting with SiH_3Cl, did not cause any appreciable disproportionation of the SiH_3Cl to occur under the experimental conditions employed

EXPERIMENTAL

All work was carried out in a Pyrex glass vacuum system The apparatus, instruments and techniques used were similar to those previously described(1 11) Mass spectra were obtained on a Consolidated 21-130 Mass Spectrometer

Commercial BCl_3 (mol wt found 118 7, calcd 117 20, infra-red spectrum identical to published spectrum(14)), and BF_3 (mol wt found 66 9 calcd , 67 81, vapour-pressure at −111 5°, found 307 mm calcd , 314 mm,(15) infrared spectrum identical to published spectrum(16) were used without further purification Disilane was obtained by the reduction of Si_2Cl_6 in di-n-butyl ether by $LiAlH_4$(17) Its purity was checked by its molecular weight (found 62 1, calcd , 62 23), and infrared spectrum(17 18) Silane was obtained as a by-product in the disilane preparation and was purified by several distillations through a trap maintained at −134 Its purity was checked by its molecular weight (found 32 1, calcd , 32 12) and infrared spectrum(19) SiH_3Cl was obtained by reacting $(SiH_3)_2O$ with BCl_3 at 78° for 12 hr(20) and was purified by distillation through a trap held at 126° Its purity was checked by its molecular weight (found 67 1, calc 66 57) and infrared spectrum(21)

Silane and boron trichloride Silane (0 0459 g 1 43 mmole) and BCl_3 (0 0606 g, 0 517 mmole) were distilled into a 200 ml bulb and were held at 0 for 12 5 hr No liquid phase was present An infra-red spectrum of the mixture indicated that only the starting materials were present Silane (0 0465 g, mol wt found 32 5, calc , 32 12, infra-red spectrum identical to that of pure compound(19)) was separated from BCl_3 (0 0598 g, mol wt found 117 7, calc 117 20, confirmed by infra-red spectrum(14)) by distillation through a trap held at −134 The combined weights of the materials recovered corresponded to 99 8 per cent of the combined weight of the reactants

Silyl chloride and boron trichloride Silyl chloride (0 0295 g 0 443 mmole) and BCl_3 (0 0268 g, 0 229 mmole) were distilled into a 200 ml bulb and held at 0 for 12 5 hr No liquid phase was present

---

(11) I G L WARD and A G MACDIARMID, *J Amer Chem Soc* **82**, 2151 (1960)

(12) M ABEDINI, C H VAN DYKE and A G MACDIARMID *J Inorg Nucl Chem* **25**, 307 (1963)

(13) K S PITZER and R K SHELINE, *J Chem Phys* **16**, 552 (1948), P H LEWIS and R E RUNDLE *ibid* **21**, 986 (1953)

(14) R E SCRUBY, J R LACHER and J D PARK *J Chem Phys* **19**, 386 (1951)

(15) O RUFF and O BRETSCHNEIDER, *Z Anorg Chem* **206**, 59 (1932)

(16) C R BAILEY, J B HALE and J W THOMPSON, *Proc Roy Soc* A **161**, 107 (1937)

(17) G W BETHKE and M K WILSON *J Chem Phys* **26**, 1107 (1957)

(18) H S GUTOWSKY and E O STEJSKAL, *J Chem Phys* **22**, 939 (1954)

(19) C H TINDAL, J W STRALEY and H H NIELSEN, *Phys Rev* **62**, 151 (1942)

(20) M ONYSZCHUK, *Canad J Chem* **39**, 808 (1961)

(21) C NEWMAN, J K O'LOANE, S R POLO and M K WILSON, *J Chem Phys* **25**, 855 (1956)

An infra-red spectrum of the mixture indicated that only the starting materials were present Th absence of an absorption at 877 cm^{-1},(22) indicated that no SiH_2Cl_2 had formed through the di proportionation of the SiH_3Cl

Disilane and boron trichloride Disilane (0 0970 g, 1 56 mmole) and BCl_3 (0 0868 g, 0 741 mmole) were distilled into a 200 ml bulb and were held at 0° for 12 5 hr No liquid phase was present initially, but at the end of the above period a trace of transparent deposit was observed at the bottom of the reaction vessel The reaction products were separated by means of a low temperature fractionating column similar to that described by Coates (23) Slightly impure B_2H_6 (0 0115 g, mol wt found 28 1 calc , 27 69, confirmed by infra-red spectrum(24)) was obtained at a column temperature of approximately −123 The infra-red and mass spectra of the material showed that the impurity consisted only of SiH_4 The quantity of pure B_2H_6 present, calculated from the molecular weight was 0 0103 g (0 372 mmole, 100 per cent yield) It was not possible to separate B_2H_6 and SiH_4 from each other quantitatively in the vacuum system because of the small difference in their boiling points

On allowing the residue in the fractionating column to distill slowly from a trap at −112 , slightly impure excess Si_2H_6 (0 0394 g, mol wt found 63 6, calc , 62 23, infra-red spectrum identical to that for pure Si_2H_6(17 18)) was obtained On redistillation, a sample of completely pure Si_2H_6 (mol wt found 62 0, calc , 62 23) was isolated The remaining volatile material (0 124 g, mol wt 136 0) could not be separated quantitatively in the vacuum system Its infra-red spectrum was consistent with the presence of Si_2H_5Cl(12) and $Si_2H_4Cl_2$(12) in the mixture The mass spectrum of the mixture showed the presence of Si_2H_5Cl, $Si_2H_4Cl_2$ and $Si_2H_3Cl_3$ No hydrogen was formed during the reaction The combined weights of the volatile products amounted to 95 2 per cent of the weight of the reactants

When the reaction was repeated using a 9 1 molar ratio of Si_2H_6 to BCl_3, Si_2H_5Cl and $Si_2H_4Cl_2$, but no $Si_2H_3Cl_3$ were observed in the reaction products In a 16 hr reaction at room temperature hydrogen was liberated in addition to the products stated above A considerable amount of brown viscous non-volatile material was formed in the reaction vessel In another 16 hr experiment at 78 , a reaction similar to that first described took place No hydrogen was formed, but a species was observed which rapidly decomposed to give B_2H_6 in the gas infrared cell

Disilane and boron trifluoride Disilane (0 0877 g, 1 41 mmole) and BF_3 (0 0498 g 0 734 mmole) were distilled into a 200 ml flask and were held at 0° for 12 5 hr An infra-red spectrum of the mixture indicated that only the starting materials were present The mixture was therefore held at room temperature for an additional 19 hr and after this time the infra-red spectrum indicated that no reaction had occurred Several distillations of the mixture through a trap held at 134 gave Si_2H_6 (0 0840 g, mol wt found 61 9, calc 62 23, confirmed by infra-red spectrum(17 18)) and BF_3 (0 0529 g mol wt found 67 3, calc , 67 82, infra-red spectrum(16) indicated a trace of Si_2H_6 impurity) The combined weights of the materials recovered corresponded to 99 6 per cent of the combined weights of the reactants

(22) J A HAWKINS and M K WILSON, *J Chem Phys* **21**, 360 (1953)
(23) G F COATES, *J Chem Soc* 2003 (1951)
(24) W C PRICE, *J Chem Phys* **16**, 894 (1948)

J. Inorg. Nucl. Chem. 1963, Vol. 25, pp. 136 to 138. Pergamon Press Ltd. Printed in Northern Ireland

LETTERS TO THE EDITORS

The structures of ZnLiVO$_4$ and ZnLiNbO$_4$

(*Received* 17 *May* 1962)

IN the course of an investigation of compounds with ordered spinel structure we tried to prepare zinc lithium vanadate and niobate (ZnLiVO$_4$ and ZnLiNbO$_4$).

An intimate mixture of high-purity lithium carbonate Li$_2$CO$_3$, zinc oxide ZnO and vanadium (or niobium) pentoxide V$_2$O$_5$ (Nb$_2$O$_5$) was fired for 24 hr at 700°C (at 1000°C respectively) in an atmosphere consisting of a mixture of equal parts of oxygen and carbon dioxide. X-ray powder diagrams of the reaction products were obtained with CoKα radiation on a "Norelco" diffractometer.

ZnLiVO$_4$

This compound has recently been prepared by DURIF.[1] Our results are in agreement with those reported. ZnLiVO$_4$ has phenacite structure with $a = 14.18$ Å and $c = 9.486$ Å (DURIF's values are 14.10 Å and 9.498 Å respectively). Remembering that cobalt and nickel lithium vanadate (CoLiVO$_4$ and NiLiVO$_4$) have spinel structure[2] and that in the phenacite structure the anions do not form a close packing as is the case in the spinel structure, it seemed worth while trying to transform the phenacite phase of ZnLiVO$_4$ into a spinel phase by pressure. We succeeded in bringing about this transformation by keeping the sample for 32 hr under a pressure of 30 kb at a temperature of 400°C, using a simple squeezer apparatus as described in reference[3], cooling under pressure to room temperature and finally removing the pressure. Up till now only olivine-spinel transformations have been reported.[4] As far as we know this is the first example of a phenacite-spinel transformation. The X-ray diagram of the spinel phase of ZnLiVO$_4$ shows the well-known spinel reflections without any superstructure reflections. The cell edge is $a = 8.309$ Å. From a calculation of the intensities of the reflections we conclude that the cation distribution is V[LiZn]O$_4$, the pentavalent vanadium ions occupying the tetrahedral sites. From the cell dimensions of the phenacite and the spinel phase of ZnLiVO$_4$ their densities can be calculated. These appear to be 3.39 and 4.34 respectively.

ZnLibNbO$_4$

From the X-ray diagram of zinc lithium niobate it follows that the unit cell of this compound is tetragonal with lattice parameters $a = 6.082$ Å and $c = 8.402$ Å ($c/a = 1.38$). Another unit cell is possible however, this one being a slightly tetragonally deformed cube with lattice parameters $a = 8.602$ (i.e. $6.082 \times \sqrt{2}$) Å and $c = 8.402$ Å ($c/a = 0.977$). Using this latter unit cell the X-ray diagram shows the reflections of a tetragonally deformed spinel phase with a number of superstructure lines. The real structure of ZnLiNbO$_4$ could not be deduced with sufficient accuracy from the powder diagram.

We tentatively assume that the structure of ZnLiNbO$_4$ can be described as a tetragonally deformed spinel structure with cation distribution Zn[LiNb]O$_4$ and a 1 : 1 order of Li$^+$ and Nb^{5+} in the octahedral sublattice. A calculation of the intensities of the spinel reflections based on this cation distribution was in good agreement with the experimental values. Calculating the intensities of the superstructure reflections, the experimental values agree most satisfactorily with a model in which the rows of octahedral sites in the [110] and [$\bar{1}$10] directions are occupied in the sequence Li-Nb-Li-Nb and the rows in the [101], [$\bar{1}$01], [011] and [0$\bar{1}$1] directions in the sequence Li-Li-Nb-Nb. This superstructure was proposed some years ago as one of the possible reasons for the tetragonality of copper ferrite.[5] Afterwards this appeared to be a misconception. The superstructure of ferrous ferrite

---

[1] A. DURIF, *Bull. Soc. franç. Minér. Crist.* **84**, 322 (1961).

[2] J. C. BERNIER, P. POIX and A. MICHEL, *C. R. Acad. Sci.* **253**, 1578 (1961).

[3] D. T. GRIGGS and G. C. KENNEDY, *Amer. J. Sci.* **254**, 722 (1956).

[4] See e.g. A. E. RINGWOOD and M. SEABROOK, *Nature (Lond.)* **193**, 158 (1962).

[5] F. PRINCE and R. G. TREUTING, *Acta Cryst.* **9**, 1025 (1956).

J. Inorg. Nucl. Chem. 1963. Vol. 25. pp. 1507 to 1514. Pergamon Press Ltd. Printed in Northern Ireland

WATER ASSOCIATED WITH THE EXTRACTION OF TRIS (4,7-DIPHENYL-1,10-PHENANTHROLINE) IRON(II) CHELATE INTO CHLOROFORM, NITROBENZENE AND 1-DECANOL

D. R. Gere* and C. E. Meloan

Department of Chemistry, Kansas State University, Manhattan, Kansas

(*Received 8 October* 1962, *in revised form* 22 *April* 1963)

Abstract—The number of molecules of water associated with Tris(4,7-diphenyl-1,10-phenanthroline) Iron(II) chelate was found to be 57.0 ± 6 per molecule of chelate. The same results were obtained obtained whether the species was extracted into chloroform, nitrobenzene or 1-decanol. Likewise no change was observed whether the associated anion was sulphate, perchlorate or chloride.

Meloan and Brandt[(1)] measured the number of water molecules associated with the benzohydroxamic acid chelates of uranium (VI) and iron (III) when extracted into 1-decanol. A general relationship was established between the amount of water normally soluble in a given alcohol and the amount of chelate extracted into that alcohol. They found 6 ± 1 molecules of water associated with the uranium (VI) chelate and 9 ± 3 associated with the iron (III) chelate.

Although this was the first published account of the measurement of water associated with extracted chelates, Swift and Axelrod[(2)] had been interested in this idea in 1940, relative to the extraction of ferric chloride into ether from aqueous solution. This sort of information has been sought more recently in the field of inorganic extractions such as the extraction of hydrated acids described by Tuck and Diamond[(3)]. More recently Gere and Meloan[(4)] found 5 ± 2 molecules of water associated with the bis(8-quinolinol)dioxouranium(VI) chelate extracted into chloroform.

It was felt that the work on extracted chelates should be extended to see if the association of water molecules was present only with neutral chelate extractions or if this also occurred with ion-association chelate extractions.

The tris(4,7-diphenyl-1,10-phenanthroline)iron(II) chelate was selected, first because this chelate system differs from the previoulsy mentioned systems in that the ligand co-ordinates through the unpaired electrons on heterocyclic nitrogen atoms with retention of the same charge of the uncomplexed metal ion on the formed chelate. A second reason for choosing this system was that it could be extracted into a variety of solvents, a distinct advantage over the previous chelates. A third reason was that the basic phenanthroline molecule has many known derivatives which would allow further correlation studies if required

---

* Abstracted from a thesis submitted by D. R. Gere to the graduate school of Kansas State University, May 1962, in partial fulfillment of the requirements for the degree of Master of Science.

(1) C. E. Meloan and W. W. Brandt, *J. Inorg. and Nucl. Chem.* **24**, 1645 (1963).

(2) E. H. Swift and J. Axelrod, *J. Amer. Chem. Soc.* **62**, 33 (1940).

(3) D. G. Tuck and R. M. Diamond, *J. Phys. Chem.* **65**, 193 (1961).

(4) D. Gere, and C. E. Meloan, *J. Inorg. Nucl. Chem.* 117, (1963).

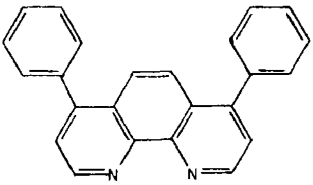


FIG 1

The structure of 4,7-diphenyl-1 10-phenanthroline is shown in Fig 1

This type of ligand forms a 3 1 chelate with iron(II) which has the following octahedral configuration (Fig 2)

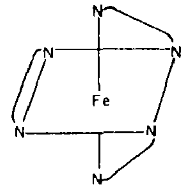


FIG 2

This system enabled the change of anions while maintaining the chelate cation intact throughout a series of analogous extraction measurement experiments

EXPERIMENTAL

Apparatus

Beckman model DB spectrophotometer All spectrophotometric data were obtained using a Model DB recording spectrophotometer equipped with matched 1 00 cm silica cells

KF-3 aquameter A Beckman KF-3 aquameter was used for the automatic titration of the water using the dead stop endpoint detection system The KF-3 permitted the method to be free of human error inherent in colour judging, eliminated distinguishing between true and false endpoints, and permitted the titration of coloured solutions

pH measurements All pH measurements were made using either a Beckman Zeromatic or a Beckman Model N pH meter

Reagents

The dry methanol, the standard water solution, pyridinium iodide and the Karl Fischer reagent were prepared as described by MELOAN and BRANDT(1)

Water Ion-free water was prepared by running distilled water through a column of mixed bed ion exchange resins, previously treated to insure water with a specific resistance of greater than 10^6 Ω/cm, as described by SAMUELSON (5)

1-*Decanol* This alcohol, as well as all of the other alcohols was distilled in an all glass still just prior to use to remove peroxides which destroy the chelate (6)

Nitrobenzene Reagent grade nitrobenzene was used without any further treatment An infrared spectrum of the nitrobenzene was obtained with a Perkin Elmer Model 237 Spectrophotometer When compared to a standard spectrum, no impurity bands were found

Standard ion solution A 0 0100 M iron solution was prepared by weighing out 0 5585 g of 99 9 per cent iron wire and transferring to a 500 ml conical flask Five ml of concentrated acid (dependent upon the anion desired) and 30 ml of de-ionized water were added Gentle heat was applied to dissolve the wire and the solution was allowed to cool. The solution was then transferred to a 1000 ml volumetric flask and diluted to the mark with de-ionized water.

---

(5) O SAMUELSON, *Ion Exchangers in Analytical Chemistry* p 259 Wiley, New York (1956)

(6) C E MELOAN Doctoral Thesis, Purdue University (1959)

0.01 *M 4,7-diphenyl-1,10-phenanthroline* $C_{24}H_{16}N_2$, *mol. wt.*, 332.41. A 0.01 M solution of this compound was prepared by dissolving the compound in 50 ml of absolute ethanol and diluting the solution with 50 ml of H_2O. Alternately, 1-decanol was used as the solvent.

Hydroxylammonium chloride, 10 per cent aqueous solution. Ten grams of reagent grade hydroxyl ammonium chloride was dissolved in 100 ml of water. The solution was then placed in a 125 ml conical separatory funnel and 1 ml of 0.01 M 4,7-diphenyl 1,10-phenanthroline was added. Ten ml of chloroform was added and the funnel shaken. Allowing time for the phases to separate, the lower red chloroform layer was drawn off. The red colour was due to formation of the iron(II) chelate. The iron was present as an impurity in the hydroxylammonium chloride. The procedure was repeated until the chloroform layer was colourless, usually one extraction was all that was necessary to render the reagent iron-free.

Sodium acetate buffer. A 10 per cent aqueous solution was prepared by dissolving 10 g of the trihydrate in 100 ml of water. This solution was rendered iron-free and copper-free by the process used for hydroxylammonium chloride.

Method

The method used throughout the entire investigation was essentially that of MELLON and BRANDT[1] with suitable variations when necessary. The Karl Fischer Reagent technique as described by MEYERS *et al.*[7] (5) was used to measure the amount of water present in the organic solvents.

The amount of water in the organic solvent was determined with the aqueous phase containing all components except the chelate itself. This comprised the blank determination. Solutions were then made up containing varying concentrations of the chelate in the organic phase. The amount of water was determined in the organic phase of each of the concentrations. The number of moles of water present in a given volume of organic phase was plotted against the number of moles of chelate present in the same given volume of organic phase (see Fig. 3). The concentration of chelate present was determined spectrophotometrically.

A least squares determination was then applied to the data to obtain the slope of the straight line into which the data developed. This slope yielded the mole ratio of water molecules to chelate molecules in the organic phase. The intercept of the straight line gave the solubility of water in the organic solvent at zero concentration of chelate.

Procedure

The procedure followed for the formation of these chelates was essentially that of DIEHL and SMITH[8] in their booklets concerning the chemistry of ferroin chelates. The chelate formation took place in the aqueous phase and when complete, the extracting solvent was then added and the extraction proceeded as in the bis(8-quinolinol)dioxouranium(VI) method.[4]

The ligand was either dissolved in water or in the case of low solubility, prepared in ethanol-water solutions. In some instances the ethanol changed the experimental conditions in that it increased the solubility of water in certain organic solvents. If this condition arose, the ligand was prepared as a solution using the extracting solvent as the ligand solvent. Alternately, the ligand was added to the aqueous phase as a solid. In the latter two cases each chelate sample was analysed spectrophotometrically.

It was important to note that in each experiment a different order of concentrations was used in obtaining the raw values. That is, one time the least concentrated chelate solution was prepared titrated first followed by the next most concentrated solution proceeding in order of increasing concentrations to the final concentration. Another time the order would be completely reversed and then random selection was used.

At least two and sometimes more solution blanks were prepared and titrated with each experiment. Usually one blank would be run initially and the second blank would be run after all of the chelate

---

[7] R. J. MEYERS, D. E. METZLER and E. N. SWIFT, *J. Amer. Chem. Soc.* **72**, 3767 (1950).

[8] H. C. DIEHL and G. F. SMITH, *The Iron Reagents: Bathophenanthroline, 2,4,6-Tripyridyl-s-Triazine and Phenyl-2-Pyridyl Ketoxime*. Columbus, Ohio: The G. Frederick Smith Chemical Company, 1960.

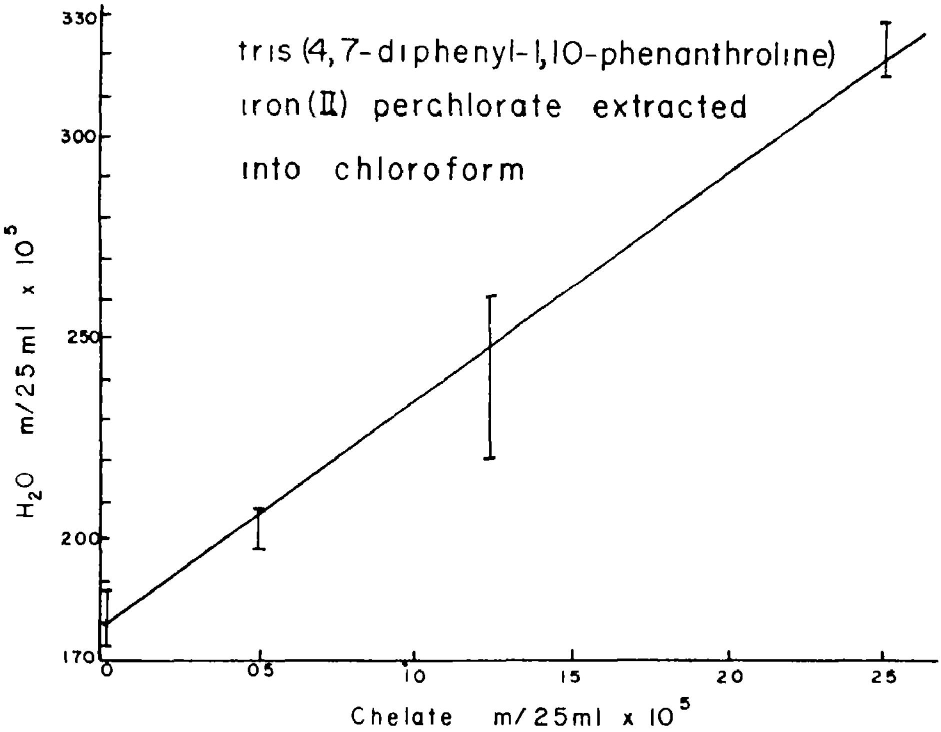


FIG 3

solutions had been prepared and titrated This was not a strictly adhered to technique however This was because there was usually no detectable difference between the blank solutions run at different times

Another procedure followed was the preparation of reagents The usual method followed was to prepare each reagent freshly for each experiment with the exception of the standard metal ion solutions This would preclude any error due to miscalculation of any concentrations

Dielectric constant measurement A calibration chart was prepared by plotting instrument readings of the Sargent Chemical Oscillometer vs dielectric constant values were obtained from MORRISON and FREISERS book (9)

RESULTS AND DISCUSSION

Extraction of tris(4,7-diphenyl-1,10-phenanthroline) iron(II) chelate

Knowing that some "neutral" chelates, extracted into alcohols and organic solvents such as chloroform, carried waters of association along with them, it was felt that ion-association chelate systems should be looked into to see if this phenomena was also present there

It was felt that the "ferrion" chelate systems would present a good starting point because the chemistry of the entire family of chelates had been so well worked out previously Another factor considered in this choice was the fact that the chelates extracted quite well Some of the distribution ratios are as high as 3600 (8) In addition it was known that this chelate was extractable into at least three different solvents namely, 1-decanol, chloroform and nitrobenzene

---

(9) G H MORRISON and H FREISER, *Solvent Extraction in Analytical Chemistry* J Wiley, New York (1957)

It was found that the tris(4,7-diphenyl-1,10-phenanthroline)iron(II) sulphate ion-association chelate extracted into chloroform along with 56 ± 4.0 molecules of water. Table 1 gives the results for the calculation of the slope of the plot of chelate concentration vs. water concentration by the least squares method.

TABLE 1—RESULTS OF A LEAST SQUARES DETERMINATION OF THE NUMBER OF WATER MOLECULES ASSOCIATED WITH TRIS(4,7-DIPHENYL-1,10-PHENANTHROLINE IRON(II)

Anion	Solvent	Results (based on a minimum of 15 individual determinations)
SO_4^{2-}	Chloroform	56 ± 4
ClO_4^-	Chloroform	56 ± 4
Cl^-	Chloroform	61 ± 4
SO_4^{2-}	Nitrobenzene	53 ± 5
ClO_4^-	Nitrobenzene	56 ± 5
Cl^-	Nitrobenzene	59 ± 5
SO_4^{2-}	1-decanol	60 ± 10
ClO_4^-	1-decanol	68 ± 10
Cl^-	1-decanol	48 ± 10
	Chloroform alone	1.3 mg/ml
	Nitrobenzene alone	2.9 mg/ml
	1-decanol alone	40.0 mg/ml

It was of interest that much greater concentrations of chelate were used here than with the bis(8-quinolinol)dioxouranium(VI) system.⁽¹⁾ The concentration was so great in fact that in some of the more concentrated solutions, the chelate precipitated out of aqueous solutions. This, however, had no effect of the results. As soon as the organic solvent was added and shaking of the separatory funnel commenced, the solid precipitate dissolved in the organic solvent. It was observed that this was essentially an instantaneous dissolution in that the aqueous phase was completely clear and colorless by the fifth inversion.

The concentration of chelate in the organic phase in most instances was assumed to be the theoretical amount of chelate formed from addition of stoichiometric amounts of metal and ligand standard solutions. It is known⁽⁸⁾ that the tris(4,7-diphenyl-1,10-phenanthroline iron(II) chelates have large formation constants and a distribution ratio of 3600. The large distribution ratio predicts a completely quantitative extraction with one stage or theoretical plate.

In cases of doubt, such as when the extraction solvent served as the ligand solvent, and when the ligand was added as a solid, the concentrations were obtained by measuring the absorbance of a 1:10 aliquot of the organic phase and using a Beer's Law calculation based on published values of the molar absorptivity. This technique was applied in known and suspected cases of addition of excess ligand or metal ion solutions also.

It was observed that neither the sodium acetate buffer, hydroxylammonium chloride, excess iron (II) solution, excess 4,7-diphenyl-1,10-phenanthroline, nor ethanol effected the water dissolved in the chloroform. This included the ligand which was completely extracted itself when uncomplexed. It is conceivable that the ligand could carry over one molecule of water in that some of the phenanthrolines are obtained commercially as the monohydrate. However, even if a one-fold excess were accidently added and extracted, this would not have added an appreciable error. There was no experimental evidence that the monohydrate was extracted however.

The previously mentioned techniques(1,4,6) such as centrifuge time and water-bath equilibrium time techniques were followed here as well. It was noted that the chelate was stable for a considerable length of time.(7)

The tris(4,7-diphenyl-1,10-phenanthroline iron(II) perchlorate and chloride were prepared and extracted into chloroform. The number of water molecules associated with each molecule of chelate were 56.0 ± 4.0 and 60 ± 4.0 respectively. The mean value for the three anion-association chelates would then be 58. Because the average deviations among a group of titrations at the same concentration for a given anion present was of higher value (approximately 4.0), one could say that a change of anion had no appreciable effect on the number of water molecules associated with each chelate.

Since the anion had little or no effect on the number of waters associated with the chelate extracted into chloroform, it was decided to extract the various anion-substituted chelates into other solvents.

The next solvent was nitrobenzene. The values for the sulphate, chloride and perchlorate chelates were 53, 57 and 56 molecules of water per molecule of chelate. These values gave a mean value of 56. It was significant that the average deviation here was less than the experiments in chloroform. The blank solubility of water in nitrobenzene was approximately three times the value in chloroform. This meant that either a large amount of Karl Fischer Reagent must be added via the pipette or a smaller aliquot of organic solvent must be taken for titration. Because of the inherent difficulties of preparing and standardizing Karl Fischer Reagent, a smaller aliquot was taken and the corresponding small amount of Karl Fischer Reagent. Ten ml aliquots were used for titration of nitrobenzene samples. It was observed that much better precision was obtained with the titrations of the nitrobenzene blank solutions than the chloroform blanks. A possible explanation for this might have been the greater presence of emulsified water in chloroform than in nitrobenzene. The two phases appeared to separate much more rapidly in nitrobenzene than in chloroform. This could possibly have been due to relative differences in specific gravity (1.203, 1.489).

The next was 1-decanol, the original solvent used by MELOAN and BRANDT.

The values in 1-decanol for the sulphate, chloride, and perchlorate chelate were 60 and 48 and 68 respectively for an average value 57 molecules of water associated with each molecule of chelate.

The poorer precision achieved in this solvent was not at all surprising considering that the solubility of water in the solvent blank was some forty times that in chloroform. A 5 ml aliquot of 1-decanol took nominally 75.00 ml of Karl Fischer Reagent compared to a nominal 12 ml Karl Fischer Reagent required for a 25.00 ml aliquot of chloroform. Thus even the blank values would be expected to have a poorer precision in 1-decanol. This may be an anion effect, however, the precision must be improved before this can be ascertained.

In the previously used extraction solvents prior to the 1-decanol experiments it was observed that the ethanol used as the ligand solvent had no effect on the number of molecules of water associated with the tris(4,7-diphenyl-1,10-phenanthroline) iron(II) chelate However, preliminary experiments indicated unbelievably high results Addition of increments of ethanol to blank solutions gave corresponding increases in the solubility of water in the decanol (See Table 2) Dielectric constant measurements confirmed the fact that at least a certain amount of ethanol was being extracted into the 1-decanol

TABLE 2 — EFFECT OF ETHANOL ON THE SOLUBILITY OF WATER IN 1-DECANOL

Sample	Ethanol by Volume (%)	Mg H_2O/5 0 ml	Dielectric constant
1	0 0	144	6 5
2	0 0	152	6 5
3	0 0	148	6 5
4	0 0	152	6 5
5	16 6	188	12 5
6	16 6	185	12 5
7	16 6	185	12 5
8	16 6	185	12 5

This difficulty was obviated by adding the ligand as a solid

Using the tris(4,7-diphenyl-1,10-phenanthroline) iron(II) perchlorate extraction as a basis of comparison, the dielectric constants of several solvents which extracted the chelate were obtained and also the dielectric constants of two solvents which failed to extract this chelate to any measurable extent Table 3 shows the results obtained

TABLE 3 DIELECTRIC CONSTANTS OF ORGANIC SOLVENTS

Solvent	Dielectric constant	H_2O solvent*	Does extract
Nitrobenzene	35 0	3 0	Yes
Methyl-phenyl	17 0	20 0	Yes
Methyl-hexyl ketone	10 0	12 0	Yes
1-Decanol	6 5	30 0	Yes
Chloroform	5 0	1 2	Yes
Amylene	2 2	0 3	No
2 2,4-trimethylpentane	1 8	0 2	No

* Solubility in terms of mg of water per ml of solvent

It was well known that the higher the dielectric constant, the better a polar compound would dissolve However, it was observed that the solubility of water in amylene was 18 10^{-5} moles of water per 10 00 ml of amylene Now if the tris(4,7-diphenyl-1,10-phenanthroline) iron(II) perchlorate would have been dissolved to the extent of 10^{3} M (a concentration obtained easily in the other solvents), it would have been expected to carry over 56×10^{-5} moles of water with it This was some three times the solubility limit This assumed that the 56×10^{5} moles of water would have been evenly distributed throughout the 10 00 ml If it was concentrated about the chelate it would explain why even one-third of this amount failed to dissolve

SUMMARY

There are 57 ± 6 molecules of water involved with the extraction of the tris(4,7-diphenyl-1,10-phenanthroline) iron(II) chelate It is not known if, say ten molecules are really bonded, and then this compound alters the dielectric of the solvent, thus allowing 40–50 more water molecules to dissolve or if in fact, all of the water is bonded to the chelate Current work is under way to attempt to answer this Regardless of where or how the water is present, the amount is fairly certain It was found that none of the compounds involved reacted with the Karl Fischer Reagent to give a false value and the experimental conditions were regulated and reproduced to the point where pH, ionic strength and temperature effects could be ruled out

J Inorg Nucl Chem 1963 Vol 25 pp 1515 to 1519 Pergamon Press Ltd Printed in Northern Ireland

POLAROGRAPHY OF ZIRCONIUM AND HAFNIUM IN ACETONITRILE

J W OLVER and J W ROSS, Jr *

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts and Department of Chemistry and Laboratory for Nuclear Science, Massachusetts Institute of Technology, Cambridge Massachusetts

Abstract Data on the polarographic behaviour of zirconium and hafnium tetrachlorides in acetonitrile, in electrolytes of tetra alkylammonium perchlorate and halide are presented The stepwise reduction of these metal ions to M (III), M (II), and M (O) is proposed and supported by the polarographic data

A LARGE number of elements including the alkali metals, alkaline earth metals, aluminum, yttrium, lanthanum, rare earth metals, titanium zirconium and hafnium give obscured or ill-defined polarographic reduction waves in aqueous media because reduction of H^+ occurs either simultaneously with or at a more positive potential than the reduction of the metal WAWZONEK and RUNNER[1] showed that alkali and alkaline earth metals all give reversible or well-developed waves in acetonitrile which is a much less acidic solvent than water KOLTHOFF and COETZEE[2] have reported the polarographic behaviour in acetonitrile of several other metals which give obscured polarographic waves in water

The purpose of this work was to investigate the polarographic behaviour of zirconium and hafnium in dry CH_3CN

EXPERIMENTAL

Reagents

Acetonitrile was purified by distillation from P_2O_5 until a polarographic residual current attributable entirely to capacitive charging current was obtained over the useful potential range of tetraethylammonium perchlorate as supporting electrolyte

Tetraethylammonium perchlorate was prepared according to the method of KOLTHOFF and COETZEE[3] The salt was dried at 60-70 in a vacuum oven and stored in a vacuum desiccator

Tetramethylammonium chloride, tetraethylammonium bromide, and tetraethylammonium iodide were obtained as polarographic grade salts from South-western Analytical Chemicals These salts were thoroughly dried in a vacuum oven and stored in vacuum desiccator

Since ionic salts of zirconium and hafnium were not appreciably soluble in acetonitrile, the covalent tetrachlorides were used Zirconium tetrachloride was obtained from Mallinckrodt Chemical Company The material was sublimed in a tube furnace and the sublimate used to prepare stock solutions of $ZrCl_4$ in dry CH_3CN Hafnium tetrachloride was prepared by the reaction of Cl_2 gas with hafnium metal in a heated tube furnace The hafnium metal was obtained from the Wah Chang Corporation and contained 3 per cent zirconium The zirconium and hafnium stock solutions in CH_3CN were standardized gravimetrically by precipitating the hydrous oxide of the metal with ammonia and igniting to constant weight

---

* Present address Orion Research Corp, Cambridge 39 Mass

[1] S WAWZONEK and M F RUNNER, *J Electrochem Soc* **99**, 457 (1952)

[2] I M KOLTHOFF and J F COETZEE *J Amer Chem Soc* **79**, 1852 (1957)

[3] I M KOLTHOFF and J F COETZEE, *J Amer Chem Soc* **79**, 870 (1957)

Apparatus and methodology

Polarograms were obtained using a Sargent Model XXI Polarograph

The reference electrode was a mercury pool placed in a solution 1M in tetraethylammonium perchlorate and containing tetraethylammonium bromide in excess of the solubility This electrode varied less than 50 mV over a two month period The resistance of the reference cell and salt bridge (1 M-tetraethylammonium perchlorate in CH_3CN) assembly was between 7,000 and 8,000 Ω and all polarograms were corrected for *iR* drop

In attempting to compare successive polarographic waves measured at widely differing potentials, the waves were corrected for the wide variation in droptime of the D M E

All solutions were deaerated with prepurified nitrogen Polarograms were determined in 0 1M tetraethylammonium perchlorate except when dependence of polarographic reductions upon halide concentrations was being investigated In those cases, halide was added as designated

RESULTS AND DISCUSSION

Polarography in perchlorate media

Typical polarograms for zirconium and hafnium are shown in Fig 1 A small sodium wave has also been inserted for comparing the potentials of reduction with the established potential for sodium (1) The current on plateaus on each of the waves is dependent upon diffusion of the electroactive species to the electrode and the polarograms do not vary with time All the waves are irreversible The rising portions

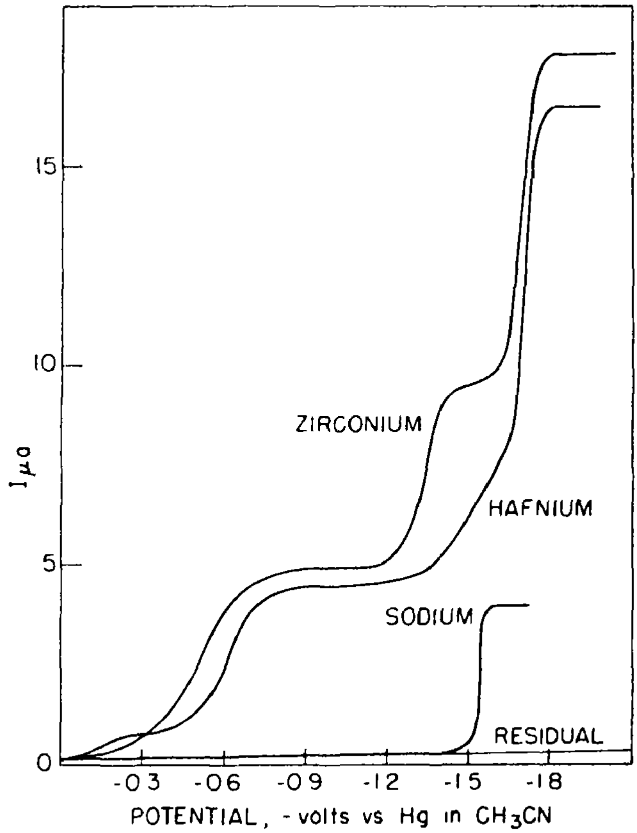


FIG. 1 —Typical polarograms of zirconium and hafnium in perchlorate media each metal approximately 2 mM

proposed by VERWEY[6] and verified by ABRAHAMS and CALHOUN[7] is quite different. At present we are trying to prepare single crystals to confirm this hypothesis.

Sincere thanks are due to Mr. C. J. M. Rooymans for performing the high pressure experiments.

Philips Research Laboratories
N. V. Philips' Gloeilampenfabrieken
Eindhoven-Netherlands
G. BLASSE

[6] E. J. W. VERWEY and P. W. HAAIJMAN *Physica* **9**, 979 (1941).
[7] S. C. ABRAHAMS and B. A. CALHOUN, *Acta Cryst.* **6**, 105 (1953).

The viscosity of liquid plutonium, predicted from a general relationship between the activation energy and melting points of metals, and the experimental data

(*Received* 5 *June* 1962)

RECENTLY[1,2,3] a simple empirical relationship was demonstrated between the melting point of a metal and the activation energy of viscous flow of the liquid metal, or $H\eta$, in cal/g atm.

With most metals the change of viscosity, η (in poises), with temperature, T(°K) can be expressed by ANDRADE's equation,[4]

$$\eta = a \exp(H\eta/RT),$$

where R = the gas constant and $H\eta$ was defined above.

The empirical relationship is based on a smooth curve obtained when the experimental $\log_{10} H\eta$ of 17 metals were plotted against the $\log_{10}$ of their melting point (in °K). The simplest manner to obtain the $H\eta$ values is to read them of the curve for a given $T_{m.p.}$. They are as follows (see Fig. 2 in ref. (3)):

$T_{m.p.}$ (°K)	$H\eta$(cal/g atm.)
300	1040
500	2000
1000	3520
1500	4520
2000	5400

This relationship has been used to predict the viscosities of liquid U, Pu and Th from their melting points to 2000°K, together with ANDRADE's expression[5] for the viscosity of a liquid metal *at its melting point*:

$$\eta_{m.p.}\ \text{(poises)} = 5.7 \times 10^{-4}\,\frac{\sqrt{A\,T_{m.p.}}}{V_A^{2/3}}\quad (A = \text{at. wt.};\ V_A = \text{At. volume at the m.p.})$$

The predicted values[1,2,3] were as follows:

Metal	U	Pu	Th
$H\eta$ (cal/g atm.)	4300	3200	5300

Recently the viscosity of liquid plutonium has been measured,[6] in the range of 648–950°C at the Mound Laboratory. Since plutonium is the *first* of the actinide elements for which experimental viscosity data are available (no data are as yet available even for the lanthanides[3]) it is of interest to compare the empirically predicted values with the experimental data. This is done in Fig. 1 where the straight line has a slope of 3200 cal/g atm. as expected from the low melting point of Pu, = 912.7°K, and the points are the experimental results of the Mound Laboratory.

The agreement is very satisfactory and leads one to expect satisfactory results with the lanthanide metals.

[1] A. V. GROSSE, *The Liquid Range of Metals and Some of Their Physical Properties at High Temperatures*. Report of the Research Institute of Temple University. September 1960.
[2] A. V. GROSSE. American Rocket Society, Space Flight Report to the Nation. New York Coliseum Oct. 9–15. 1961. Paper No. 2159–61.
[3] A. V. GROSSE *J. Inorg. Nucl. Chem.* **23**, 333 (1961).
[4] E. W. DA C. ANDRADE, *Phil. Mag.* **17**, 698 (1934).
[5] E. W. DA C. ANDRADE, *Phil. Mag.* **17**, 497 (1934).
[6] L. J. WITTENBERG, D. OFTE and W. G. ROHR, Interim Progress Report of Feb. 1961 of the Mound Laboratory, oper. by the Monsanto Chem. Co., for the U.S. Atomic Energy Commission pp. 82 and 85, see Symposium of the Amer. Soc. of Metals, Oct. 1962-Meeting.

of the initial waves are rather drawn out but a well defined plateau is reached well in advance of succeeding waves

In order to test whether the waves obtained are attributable to stepwise reductions or to reduction of complexes in sluggish equilibrium, polarograms of zirconium and hafnium were determined at concentrations varying over a thirty-fold range. The dependence of plateau currents upon concentration is shown in Fig 2 for zirconium The ratio of the current on the second plateau to the current of the first wave remains 2:1 over the range of zirconium concentrations The ratio of the total current to the current of the first wave is constant at 4:1 over the concentration range where a straight line dependence of current upon concentration exists Similar data were obtained for hafnium tetrachloride Sluggish equilibria are therefore ruled out

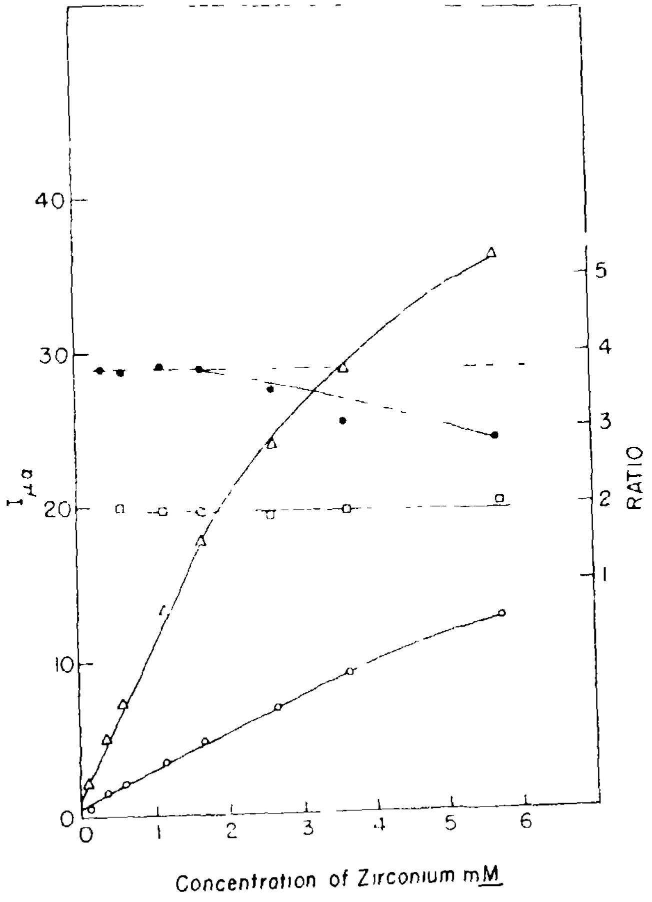


Fig. 2—Current versus concentration data for zirconium

○ —current on the first plateau

△ —current on the final plateau

□ —ratio of current on second wave to that on first wave

● —ratio of total current to current on first wave

The current concentration plots are generally curved at the higher concentrations due to breakdown of the normal diffusion process In aqueous solution polynuclear species are predominant for zirconium and hafnium at concentrations above millimolar in non-complexing media less than several molar in acid[4] Although the reduction of polynuclear species could explain much of the observed curvature, from Fig 2 curvature of current on the final plateau (which we attribute to reduction to the free metal) vs concentration must result from some other specific effect upon the diffusion process On that final wave, the shape of the current-time curve for a single mercury drop was characteristic of an adsorbed layer at high zirconium concentrations

Over the concentration range 0 3 6 mM, the half wave potentials of the first two zirconium waves were constant within the experimental limit of the reference cell stability at −0 53 and 1 33 V respectively and that of the first hafnium wave was similarly constant at −0 60 V For both metals the half-wave potential of the final wave is shifted to markedly more *negative* potentials (-1 59– 1 77 for Zr and 1 63 1 80 for Hf) as concentration of the metal increases contrary to normal behaviour of irreversibly reduced species

We propose the explanation that the polarographic waves obtained for zirconium and hafnium in CH_3CN are successive reductions to lower oxidation states All of the proposed lower oxidation states are known in the dry state and would be expected to exist in a non-acidic solvent of low solvation energy

The waves on a given polarogram are represented by

$$M(IV) + e^- \longrightarrow M(III)$$
$$M(III) + e^- \longrightarrow M(II)$$
$$M(II) + 2e^- \longrightarrow M(0)$$

The second step is well developed only for zirconium

Polarography in halide media

The effect of added halide upon the polarographic behavior of Hf and Zr was examined Solutions of I and Zr(IV) or Hf(IV) quickly turned yellow from production of I_2 and reduction of the metals to the +3 state The I_2 oxidized thiosulphate and furthermore tetraethylammonium iodide by itself remains colourless in CH_3CN over 24 hr open to air POPOV and SKELLY[5] have reported on the much greater stability of the I_3^- ion in acetonitrile over that in water which leads to a more negative reduction potential However the polarograms of the remaining Zr and Hf were unaffected by presence of I^- indicating at most very weak complex species

The effect of incremental bromide addition to a solution containing zirconium is shown in Fig 3 In excess Br , one irreversible wave representing the four electron reduction is obtained Bromide addition greatly affects the potential of Zr(IV) reduction Hafnium reacts similarly except that the reduction of the hafnium in excess bromide is more negative than the decomposition potential of the supporting electrolyte and higher bromide concentrations are necessary indicating greater stability of the zirconium-bromide species

The chloride effect is even more pronounced In only 0 01 M tetramethylammonium chloride, millimolar zirconium tetrachloride is reduced at − 1 90 V in a single

---

[4] L P VARGA Private communication (1961)

[5] POPOV and N E SKELLY, *J Amer Chem Soc* **76**, 5309 (1954)

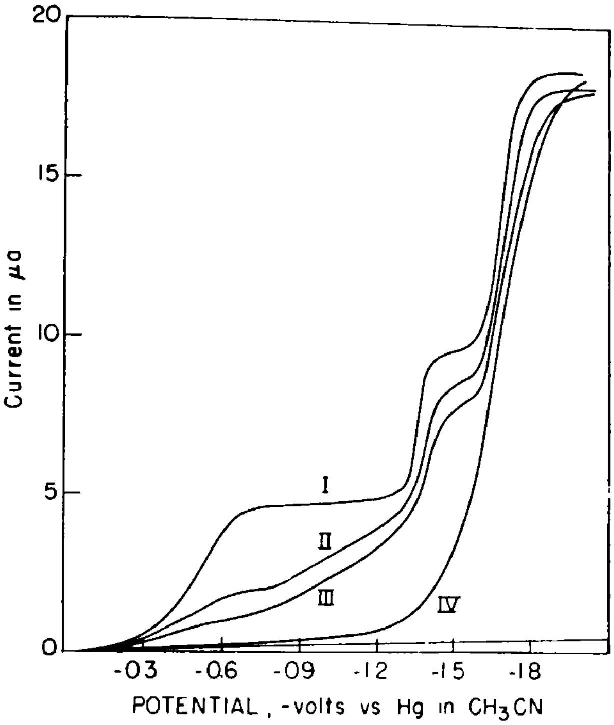


FIG. 3. Addition of bromide to zirconium.
Curve I—1.67 mM in perchlorate.
Curve II—with 0.001 M bromide added.
Curve III—with 0.002 M bromide added.
Curve IV—with 0.016 bromide added.

wave while millimolar hafnium gives no reduction wave whatsoever before the potential of decomposition of the electrolyte at −2.4 V.

Halide effects similar to these have been reported by KOLTHOFF and COETZEE[3] where for cadmium and zinc, iodide had the greatest effect on half wave potentials and chloride the least. These and the present data are consistent with observations on halide complexation data in aqueous solution for zinc and cadmium on the one hand and zirconium and hafnium on the other.[6]

That halide complexation should lead to more difficult reductions is not unreasonable. LARSON and IWAMOTO[7] have proposed a mechanism for reductions in CH_3CN which involves electron transfer through nitrile groups and halide complexation would disrupt this normal transfer process for the solvent CH_3CN.

Work designed to clarify identity of the specific complex species involved in these polarographic reductions is in progress.

Acknowledgement—Presented in part at the 140th Meeting of American Chemical Society, September 1961. Taken in part from a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Massachusetts Institute of Technology June 1961. This work was supported in part by the U.S. Atomic Energy Commission under Contract AT (30-1) 905.

[6] J. BJERRUM, G. SCHWARZENBACH and L. G. SILLEN, *Stability Constants*, Part I, Chemical Society, London (1957).

[7] R. C. LARSON and R. T. IWAMOTO, *J. Amer. Chem. Soc.* **82**, 3239 (1960).

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 1521 to 1530. Pergamon Press Ltd. Printed in Northern Ireland

CHEMICAL KINETICS OF OXYGEN EXCHANGE BETWEEN CO AND O_2

E. A. Th. Verdurmen and C. A. Bank
F.O.M.—Laboratorium voor Massascheiding, Kruislaan 407, Amsterdam 0

(*Received* 19 *December* 1962, *in revised form* 1 *May* 1963)

Abstract—In a quartz vessel at temperatures above 450°C oxygen exchange between CO and O_2 occurs as an independent process parallel to CO_2 production. The chemical kinetics of this exchange have been studied with ^{18}O as a tracer at 500°C. The oxygen exchange reaction is not influenced by the addition of water, whereas the production of CO_2 is considerably reduced. The exchange rate is only slightly enhanced by increasing the surface to volume ratio, indicating a small influence of the surface. At 500°C a rate law $S = k\,p_{CO}^{\,n}\,p_{O_2}^{\,m}$, with $n = 0.68 \pm 0.06$ and $m = 0.58 \pm 0.05$ has been found. It appeared possible to study the exchange reaction while the simultaneous CO_2 production was relatively small. It is concluded that the oxygen exchange reaction is mainly a gas-phase process whereas the formation of CO_2 occurs as a surface reaction. Exchange mechanisms are discussed.

It has been shown[1] that in a quartz vessel at temperatures above 450°C oxygen exchange between CO and O_2 occurs as an independent process parallel to the formation of CO_2. In this paper the chemical kinetics, i.e. the rate and the influence of various conditions on the rate of this exchange reaction are reported. The exchange reaction involved is characterized by a simultaneous change in the concentrations of the reactants owing to the reaction producing CO_2. We have tried to suppress the CO_2 formation in order to keep the pressures of CO and O_2 nearly constant during the time of the exchange.

EXPERIMENTAL

Gases

Natural CO was prepared by reduction of CO_2 with Zn at 400°C. Natural oxygen was taken from a gas cylinder, purity 99.5 per cent oxygen. Enriched gases were obtained by thermal diffusion in natural gases. Oxygen enriched in this way contained an appreciable amount of argon. The argon was separated from the oxygen by passing the mixture through a column of molecular sieves, as described in our previous paper.[1] The gases were purified by keeping them for several hours at liquid air temperature, they were pumped and stored. Mass spectrometric analysis showed satisfactory purity.

Apparatus

The reactions were performed in a 30 mm dia. cylindrical transparent quartz vessel (Vitreosil), volume about 100 cm³. The furnace temperature was maintained constant to ±5°C. The temperature gradient along the vessel was less than 10°C. The required vacuum (about 10^{-5} mm mercury) was obtained by a rotary oil and a mercury diffusion pump.

Procedure

Before a series of measurements the reaction vessel was first baked out for about three days at 700°C. The vessel was heated to the reaction temperature (500°C) before admitting the gas mixtures. The gases were mixed and subsequently led into the quartz vessel at the desired pressure. After reaction the gas was expanded from the vessel into a sample flask. The carbon dioxide in the samples was frozen out in liquid air, the remaining mixture CO + O_2 was collected, then the carbon monoxide was oxidized with iodine pentoxide as described previously.[1] The carbon dioxide formed by

---

[1] C. A. Bank, E. A. Th. Verdurmen, A. E. De Vries and J. J. Monterie, *J. Inorg. Nucl. Chem.* **17**, 295–301 (1961).

the I_2O_5 reaction was separated from the remaining O_2. After each experiment the ^{18}O conte
CO and O_2 was determined by conventional mass spectrometry. The precision of the ^{18}O conte
determined is between 1 and 2 per cent.

RESULTS

The amount of CO_2 formed in the reaction was found by comparing the total pressure of the gas sample and the partial pressure of the CO_2 in the same volume. The precision of the pressure readings is 0.1 mm mercury. In Tables 1 and 2 the amount of CO_2 formed in a particular experiment is given relatively to the maximum possible production of CO_2. This quantity is presented as "conversion".

Table 1.—Influence of water addition on the rate of exchange

Temperature 500°C. Total pressure 320 mm Hg.
Mixing ratio $CO : O_2$ equal to 2 : 1.
^{18}O content CO at $t = 0$: 0.635%, ^{18}O content O_2 at $t = 0$: 0.200%.

Time (min)	p_{water} (mm Hg)	Conversion (%)	$1 - F_{CO}$†	Ratio of exchange rates for wet and dry mixtures
15	-	54	0.75 ± 0.05	
15	1	21	0.79 ± 0.05	1.0 ± 0.5
15	3	16	0.84 ± 0.05	0.8 ± 0.5
15	—	46	0.79 ± 0.05	
15	1	17	0.77 ± 0.05	1.3 ± 0.6
15	3	15	0.87 ± 0.05	0.7 ± 0.4
30	—	61	0.63 ± 0.05	
30	1	31	0.62 ± 0.05	1.2 ± 0.3
30	3	24	0.71 ± 0.05	1.0 ± 0.3
60	-	78	0.43 ± 0.04	
60	1	47	0.39 ± 0.04	1.4 ± 0.2
60	3	38	0.49 ± 0.04	1.1 ± 0.2

† F_{CO} is the exchange fraction calculated from the ^{18}O contents x_0, x_t and x_∞ in CO.

Provided the reactant concentrations do not change within the exchange time the exchange rate S is defined by [(2)]

$$S = -\frac{1}{t}\frac{p_{CO}\,p_{O_2}}{p_{CO} + p_{O_2}} \ln(1 - F) \qquad \text{(a)}$$

p_{CO} and p_{O_2} signify the pressures of CO and O_2 in the reaction mixture, t is the exchange time, F is the relative exchange, or exchange fraction

$$F = \frac{x_t - x_0}{x_\infty - x_0}, \qquad \text{(b)}$$

wherein x_t is the fractional content of ^{18}O in CO or O_2, at time t, x_0 and x_∞ are th values for this fraction at $t = 0$ and $t = \infty$. The values of x_∞ have been calculat from the fractional ^{18}O content and the mixing ratio of the gas components both

---

(2) H. McKay, *Nature, Lond.* **142**, 997 (1938); *J. Amer. Chem. Soc.* **65**, 702 (1943).

TABLE 2.—INFLUENCE OF PACKING ON THE RATE OF EXCHANGE
(Surface to volume ratio increased twenty-fold)

Temperature 500°C. Total pressure 320 mm mercury
Mixing ratio CO : O_2 equal to 2 : 1
^{18}O content CO at $t = 0$: 0.635%, ^{18}O content O_2 at $t = 0$: 0.200%

Vessel	Time (min)	p_{water} (mm Hg)	Conversion (%)	F_{O_2}†	Ratio of exchange rates in packed and unpacked vessels
Unpacked	15	–	46	0.13 ± 0.02	
Packed	15	–	68	0.28 ± 0.03	2.0 ± 0.6
Unpacked	15	3	15	0.12 ± 0.02	
Packed	15	3	45	0.47 ± 0.03	4 ± 1
Unpacked	30	3	24	0.23 ± 0.03	
Packed	30	3	60	0.74 ± 0.03	4 ± 1

† F_{O_2} is the exchange fraction calculated from the ^{18}O contents x_0, x_t and x_∞ in O_2

$t = 0$. In this calculation we assumed at $t = \infty$ a proportional distribution of the ^{18}O between the gas components present at $t = 0$. A possible isotope effect was neglected.

The exchange fraction F_{CO} was calculated from the values of the ^{18}O contents in CO x_t, x_0 and x_∞. S was obtained by substitution, in expression (a), of this fraction F_{CO} and of the mean values of the partial pressures of CO and O_2 during the exchange. In all experiments, the exchange fractions F_{CO} and F_{O_2} for a particular experiment agree within experimental error. Thus the amount of ^{18}O in CO and O_2 together did not change. The exchange is accompanied by changing reactant concentrations owing to the reaction producing CO_2. Though the absence of a chemical reaction is a condition for applicability of expression (a) as a measure of exchange rate, we assume that the expression is a good approximation when the changes in concentration are relatively small. As a result of the CO_2 formation in non-stoicheiometric mixtures the mixing ratio changes with time and so does the value of x_∞. But because of the small amounts of CO_2 produced in our case (the "conversion" was always < 10 per cent for the experiments represented in Figs. 1 and 2) the value of x_∞ remains practically constant.

The dependence of the exchange rate, S, upon reactant concentrations is given in the general form

$$S = k \cdot P_{CO}^{n} \cdot P_{O_2}^{m}$$

A log–log plot of S as a function of the pressure of CO at constant O_2 pressure should give a straight line with slope n. A similar plot of S as a function of the pressure of O_2 at constant CO pressure should give a straight line with slope m. Figs. 1 and 2 are such plots for the reaction at 500°C. From the slopes of the lines in Figs. 1 and 2 a rate law $S = k \cdot P_{CO}^{n} \cdot P_{O_2}^{m}$ with $n = 0.68 \pm 0.06$ and $m = -0.58 \pm 0.05$ is found.

Calculations have been made by the method of least squares.

In Table 1 measurements are reported about the effect of water addition on the rate of CO_2 formation and the exchange rate at 500°C. By addition of water at a

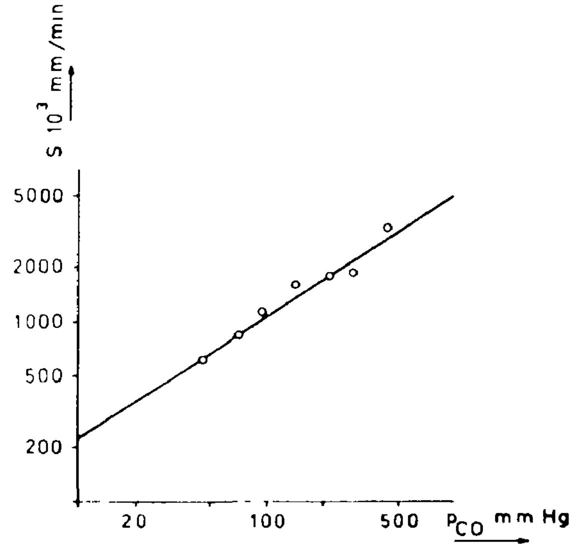


Fig. 1 —Log log plot of exchange rate S as a function of the pressure of CO, at constant O$_2$ pressure, at 500 C Slope 0 68 ± 0 06

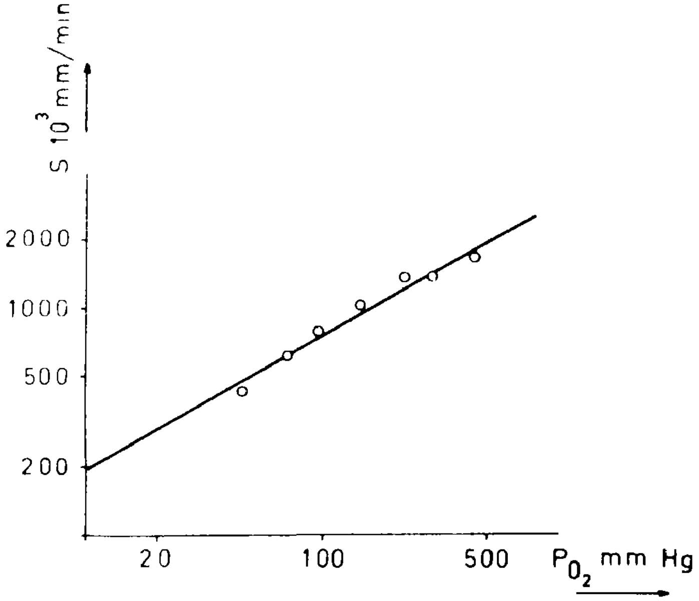


Fig. 2 —Log log plot of exchange rate S as a function of the pressure of O$_2$, at constant CO pressure, at 500 C Slope 0 58 ± 0 05

pressure of 1 mm Hg to a stoicheiometric mixture, pressure 320 mm Hg the CO$_2$ production is reduced considerably but still remains relatively high, whereas th exchange rate†, assumed to be proportional to ln (1 — F)/t, practically does n t change The further addition of water has much less influence on CO$_2$ formation a the exchange rate remains constant again

In order to test for heterogeneity, the reaction vessel was packed with crush quartz, increasing the surface to volume ratio by a factor of 20. In Table 2 measurements in a packed and unpacked vessel are compared. The rate of formation of CO_2 as well as the exchange rate are enhanced by packing the vessel. The increase in exchange rate in the mixture without added water is about a factor two. In the mixture with added water a four-fold increase was observed. These increases are considerably smaller than the change in surface to volume ratio. Studying the influence of the surface on the CO_2-producing reaction, it was observed that if the reaction vessel is kept at 600°C during months a gradual increase of rate with time occurs. This enhanced rate can probably be attributed to an increase in surface activity. The measurements on the dependence of the exchange rate upon reactant concentrations, reported in Figs. 1 and 2, were therefore performed in a vessel constructed shortly before the series of experiments started. In this vessel the rate of CO_2 production appeared to be relatively small. The exchange time in those experiments was 15–20 min.

---

† As the degree of conversion in these experiments is relatively high, owing to the changing reac concentrations only certain "mean" values of exchange rate can be compared

DISCUSSION

In a previous paper(1) it has been shown that no measureable oxygen exchange occurs below 630°C, within the reaction times used in the experiments, between any of the gases separately and the quartz of the reaction vessel. No evidence was found for CO decomposition at the wall of the reaction vessel (Boudouard equilibrium $2\,CO = C + CO_2$). Oxygen exchange between CO and CO_2, and between CO_2 and O_2 is of importance only above 800°C.(3) It appears from the data reported in our paper on CO_2 formation in mixtures of CO and O_2(5) that this reaction is mainly a surface process. The rate of CO_2 production is considerably enhanced by packing the reaction vessel with crushed quartz. Also a faster rate has been measured the longer the vessel has been baked out before introducing the gas mixture. And the rate of production of CO_2 is reduced by addition of water to the gases. It is known that water poisons the catalyst in the oxidation of CO over active oxides,(4) possibly in our experiments the retarding effect of water on CO_2 formation can be ascribed to poisoning of the quartz acting as a catalyst.

On the other hand, as can be seen from our present results, the CO–O_2 oxygen exchange rate is only slightly enhanced by packing the vessel. There is no appreciable effect of the time of bakeout. Addition of water to the gases has practically no influence on the exchange rate. So we conclude that the CO–O_2 oxygen exchange reaction is mainly a gas phase process.

As mentioned above, the dependence of the exchange rate S upon reactant concentrations is described by $S = k\, p_{CO}^{\,n}\, p_{O_2}^{\,m}$, in which the values of both n and m appear to be smaller than unity. Thus it is obvious that exchange does not occur by the simple gas reaction

$$CO + O_2 = O_2 + CO \qquad (1a)$$

A mechanism that can explain the experimental data is a bimolecular formation of an activated molecule. This activated molecule can be deactivated by collision or it may decompose to the original reactants after a certain lifetime.

In a previous paper(1) we suggested that the exchange process proceeds by way of oxygen atoms. In such an atomic mechanism two overall exchange processes have to be considered

---

(3) C. A. Bank and E. A. Th. Verdurmen, *J. Inorg. Nucl. Chem.* **25**, 667 (1963).

(4) S. Z. Roginsky, *Theoretical principles of isotope methods for investigating chemical reactions*. Moscow (1956) p. 374 review.

(5) C. A. Bank and E. A. Th. Verdurmen, *J. Phys. Chem.* (1963). To be published.

$$\mathrm{CO} + \mathrm{O} \rightarrow \mathrm{O} + \mathrm{CO} \tag{2a}$$

$$\mathrm{O} + \mathrm{O_2} \rightarrow \mathrm{O_2} + \mathrm{O} \tag{2b}$$

An average value of the experimental exchange rate is 10^{15} molec cm^{-3} sec^{-1}. As this rate depends upon both reactant concentrations, CO and O_2, the process (2b) cannot be rate determining. So the exchange rate of (2b) should be faster than 10^{15} molec cm^{-3} sec^{-1}.

In oxygen at 500°C the following reactions have to be considered

$$\mathrm{O_2} + \mathrm{M} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \mathrm{O} + \mathrm{O} + \mathrm{M} \tag{4}$$

$$\mathrm{O} + \mathrm{O_2} + \mathrm{M} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \mathrm{O_3} + \mathrm{M} \tag{5}$$

$$\mathrm{O_2} + \mathrm{O_2} \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} \mathrm{O_3} + \mathrm{O} \tag{6}$$

The exchange process (2b) can be achieved by reactions (5). The rate constants k_5 and k_{-5} have been measured by BENSON and AXWORTHY(6): $k_5 = 2.6 \times 10^7 T \exp(600/RT)$ l^2 mole^{-2} sec^{-1}, $k_{-5} = 2.0 \times 10^{12} \exp(-24000/RT)$ l mole^{-1} sec^{-1}. These rate constants reduce to the values at 500°C

$$k_5 = 1.1 \times 10^{-34}\ \mathrm{cm^6\ molec^{-2}\ sec^{-1}}$$

$$k_{-5} = 0.7 \times 10^{-15}\ \mathrm{cm^3\ molec^{-1}\ sec^{-1}}$$

At a pressure of O_2 equal to $\frac{1}{2}$ atm (i.e. $[O_2] = 1.3 \times 10^{19}$ molec cm^{-3}) in order to obtain an O/O_2 exchange rate faster than 10^{15} molec cm^{-3} sec^{-1}, the minimum O atom concentration can be calculated to be 5×10^{10} atoms cm^{-3}. Possibly also a direct exchange reaction occurs

$$\mathrm{O} + \mathrm{O_2} \rightarrow \mathrm{O_2} + \mathrm{O} \tag{5'}$$

The rate constant k_5' is not known. But if we assume an activation energy of zero and a frequency factor equal to the collision number, than an upper estimate is $k_5' \approx 10^{-10}$ cm^3 molec^{-1} sec^{-1}. In that case a minimum O atom concentration can be calculated: $[O] = 10^6$ atoms cm^{-3}.

The rate constants of reactions (6) were determined(6) to be

$$k_6 = 6.7 \times 10^9 \exp(-99200/RT)\ \mathrm{l\ mole^{-1}\ sec^{-1}},$$

and

$$k_{-6} = 3.0 \times 10^{10} \exp(-6000/RT)\ \mathrm{l\ mole^{-1}\ sec^{-1}}$$

Also an estimate of the value of k_4 was made: $k_4 = 3.5 \times 10^{13} \exp(-117000/RT)$ l mole^{-1} sec^{-1}. The rate constant k_{-4} has been measured by REEVES *et al.*(7): $k_{-4} = 2.7 \times 10^{-33}$ cm^6 molec^{-2} sec^{-1} and it is independent of temperature. At 500°C and oxygen pressure equal to $\frac{1}{2}$ atm, the rates S_4 and S_6 are

$$S_4 = k_4[\mathrm{O_2}][\mathrm{M}] = 2.7 \times 10^{-2}\ \mathrm{molec\ cm^{-3}\ sec^{-1}}$$

$$S_6 = k_6[\mathrm{O_2}][\mathrm{O_2}] = 4.8 \times 10^{-1}\ \mathrm{molec\ cm^{-3}\ sec^{-1}}$$

Thus reactions (4) and (6) cannot lead to an O/O_2 exchange with a sufficiently

---

(6) S. W. BENSON and A. E. AXWORTHY, *J. Chem. Phys.* **26**, 1718–1726 (1957).

(7) R. R. REEVES, G. MANNELLA and P. HARTECK, *J. Chem. Phys.* **32**, 632–633 (1960).

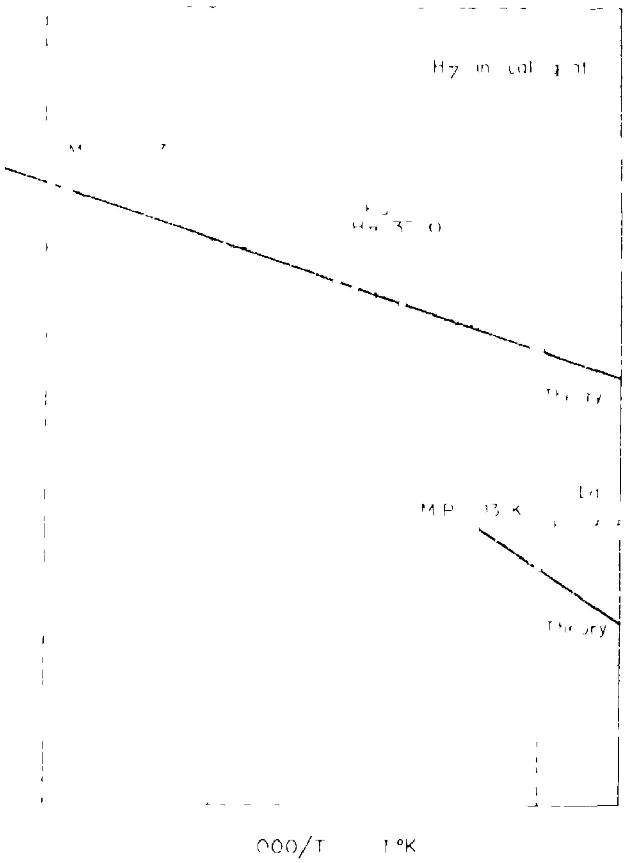


Fig. 1

In Fig. 1 we used the experimental value of η m.p. = 6.00 centipoise. The ANDRADE expression gave a value = 4.51 centipoise, or ~25 per cent too low.

The viscosity of plutonium η_{Pu} in poises, at a temperature T K, is expressed by the equation

$$\eta_{Pu} = 10.29 \times 10^{-3} \exp(3200/RT)$$

Using the melting points of the lanthanides as given by SPEDDING and DAANE[7] in their latest book *The Rare Earths*, the $H\eta$ of all rare earth metals can be estimated. The values for the first six metals are as follows:

	Melt. point (K)	$H\eta$ (cal/g atm.)
La	1193	3850
Ce	1068	3550
Pr	1208	3800
Nd	1297	4100
Sm	1345	4200
Eu	1099	3550

The predicted viscosity line for La with a slope or $H\eta$ = 3850, is also shown in Fig. 1.

Acknowledgments are due to Mr. Lerroy V. Jones of the Monsanto Research Corporation for letting us have the data on liquid plutonium.

A. V. GROSSE

Research Institute of Temple University
Philadelphia, Pennsylvania

---

(7) F. H. SPEDDING and A. H. DAANE, *The Rare Earths*, p. 179. Wiley, New York, 1961.

rate. The oxygen atom concentration in pure oxygen in thermodynamic equilibrium at 500°C is 5×10^5 atoms cm^{-3}. So that on the basis of this concentration oxygen exchange via reaction 5 is certainly too slow. However, one cannot exclude reaction 5′ as a possible O/O_2 exchange mechanism.

But the minimum O atom concentrations calculated above, should be attained within the reaction times of the experiments (15–20 min). As oxygen was heated from room temperature, where there are practically no atoms in the gas, to 500°C, the reactions producing O atoms must be relatively fast. Obviously reactions (4) and (6) are much too slow for this purpose. A suggested[(1)] mechanism for oxygen exchange in CO–O_2 mixtures is

$$CO + O \xrightarrow{k_1} CO_2^* \tag{1}$$

$$CO_2^* \xrightarrow{k_2} CO + O \tag{2}$$

$$CO_2^* + M \xrightarrow{k_3} CO_2 + M \tag{3}$$

$$CO_2^* + O_2 \xrightarrow{k_3'} CO_2 + O + O \tag{3'}$$

O atoms are formed from O_2 in reaction (3′). A calculation of a stationary state concentration for O atoms, considering this set of reactions in addition to reactions (4), (5) and (6), with certain assumptions for the values of the rate constants k_1, k_2, k_3 and k_3', shows this concentration to be considerably smaller than the stationary state concentration for O atoms in pure oxygen gas at 500°C. So it appears likely that the minimum O atom concentrations are not attained in this way. But it is reasonable to consider additionally the formation and recombination of O atoms at the wall of the reaction vessel, reactions (7)

$$O_2 + W \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} O + O + W \tag{7}$$

We have no data about k_7, the formation of O atoms from O_2 at a quartz surface. A value of k_{-7} can be obtained from data by LINNETT *et al.*[(8)] and the dimensions of our vessel: $k_{-7} = 3.3 \times 10^2$ sec^{-1}. The formation of O atoms by reaction (7) has to be fast enough to give a sufficiently high O atom concentration in a comparatively short time.

Since a heterogeneous process is now invoked, stationary state concentrations are not necessarily equal to thermodynamic equilibrium concentrations.

A stationary state concentration of O atoms can be calculated considering reactions (1), (2), (3), (3′), (5) and (7). The recombination in (7) is a first order process[(7)], so $S_{-7} = k_{-7}[O]$. Substituting $S_7 = k_7[O_2]$, an expression of the following form is obtained

$$[O] = \frac{k_7[O_2]}{\dfrac{k_1k_3[CO][M]}{k_2 + k_3[M] + k_3'[O_2]} + k_{-7}} \tag{d}$$

It was found that an expression for the CO/O_2 exchange rate S consistent with experimental data, could be obtained only by assuming that the O atom concentration

---

[(8)] J. W. LINNETT and D. G. H. MARSDEN, *Proc. Roy. Soc.* A 234, 489–504, 504–515 (1956); J. C. GREAVES and J. W. LINNETT, *Trans. Faraday Soc.* **55**, 1355–1361 (1959).

is practically determined by the O_2 concentration

$$[O] \approx \frac{k_7}{k_{-7}} [O_2] \tag{e}$$

So our experimental results indicate that the first term in the denominator of *(d) should be essentially smaller than k_{-7}. The magnitude of this term depends on the value of k_1*

Avramenko and Kolesnikova[9] *measured the overall rate constant of the process* $CO + O + M \xrightarrow{k} CO_2 + M$ and argued that this quantity is the rate constant of the reaction $CO + O \xrightarrow{k_1} CO_2^*$. Their value reduces at 500 °C to $k_1 = 1.2 \times 10^{-14}$ cm³ molec⁻¹ sec⁻¹. According to Kaufman[10] this measured k is too high and Clyne and Thrush[11] found an upper limit for this rate constant that is considerably lower. If we adopt their k value as a measure of k_1, we obtain at 500 °C $k_1 = 5.5 \times 10^{-17}$ cm³ molec⁻¹ sec⁻¹. With such a small value of k_1, and assuming upper limits for $k_2 = 10^{9}$ sec⁻¹, $k_3 = k_3' = 10^{-10}$ cm³ molec⁻¹ sec⁻¹, the first term in the denominator of (d) is found to be small with regard to k_{-7}

If reaction (2) is the rate determining step in the set of reactions (1), (2), (3), (3′) (5) and (7) an expression for the CO/O_2 exchange rate consistent with experimental data can be derived, assuming that a stationary state for the concentration of CO_2^* is attained and relation (e) holds

$$S = \frac{k_1 k_2 [CO][O_2]}{k_2 + k_3[M] + k_3'[O_2]} \frac{k_7}{k_{-7}} \tag{f}$$

From this expression one can easily show, noting that $[M] = [CO] + [O_2]$,

$$\frac{[CO][O_2]}{S} = \frac{1}{k_1 \frac{k_7}{k_{-7}}} + \frac{k_3}{k_1 k_2 \frac{k_7}{k_{-7}}} [CO] + \frac{k_3 + k_3'}{k_1 k_2 \frac{k_7}{k_{-7}}} [O_2] \tag{g}$$

Experimentally a linear relation between $[CO][O_2]/S$ and $[CO]$, and $[O_2]$ respectively has been found with reasonable agreement, as can be seen from Figs 3 and 4

From the slopes of the lines in the plots, and the intercept of the line in Fig 4 for $[O_2] = 0$, a value for $k_1 k_7/k_{-7}$ can be obtained of the order of 10^{-23} cm³ molec⁻¹ sec⁻¹. If relation (e) holds and the value of $k_1 \approx 10^{-17}$ is substituted, the O atom concentration in the experiment can be calculated $[O] \approx 10^{13}$ atoms cm⁻³. Though a higher value of the rate constant k_1 would lead to a smaller [O] value, this mechanism still requires a considerably higher number of O atoms per cm³ than can be expected from the thermodynamic equilibrium concentration in oxygen ($\approx 10^6$ atoms cm⁻³)

In our previous paper[1] we mentioned two other sets of reactions via atomic oxygen a mechanism wherein CO_2^* is formed in a termolecular reaction $CO + O + M \rightarrow CO_2^* + M$, and the mechanism suggested by Harteck and Dondes[12] reaction via C_2O and C_3O_2 formed from CO^* produced in $CO + O + CO \rightarrow CO_2 + CO^*$. Neither of these mechanisms leads to an expression consistent with experimental data

---

[9] L. I. Avramenko and R. V. Kolesnikova, *Bull Acad Sci Div Chem Sci* 1506–1513 (19 *Isvest Akad Nauk USSR Otdel Khim Nauk* 561–563 (1960)

[10] F. Kaufman, *Progress in reaction kinetics* 1, 1–39 (1961)

[11] M. A. A. Clyne and B. A. Thrush, *Proc Roy Soc* A **269**, 404–418 (1962)

[12] P. Harteck and S. Dondes, *J Chem Phys* **27**, 1419 (1957)

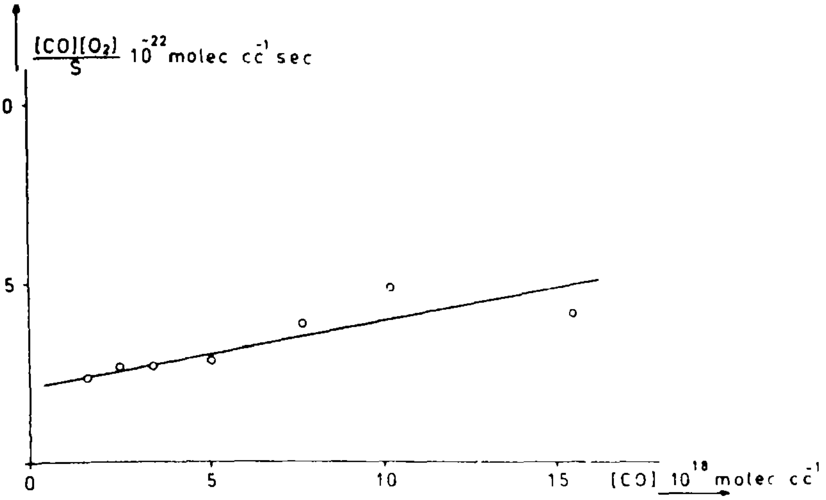


FIG. 3 Variation of the quantity $\frac{[CO][O_2]}{S}$ with CO concentration, at constant O_2 concentration at 500 C Slope 0 16 0 04

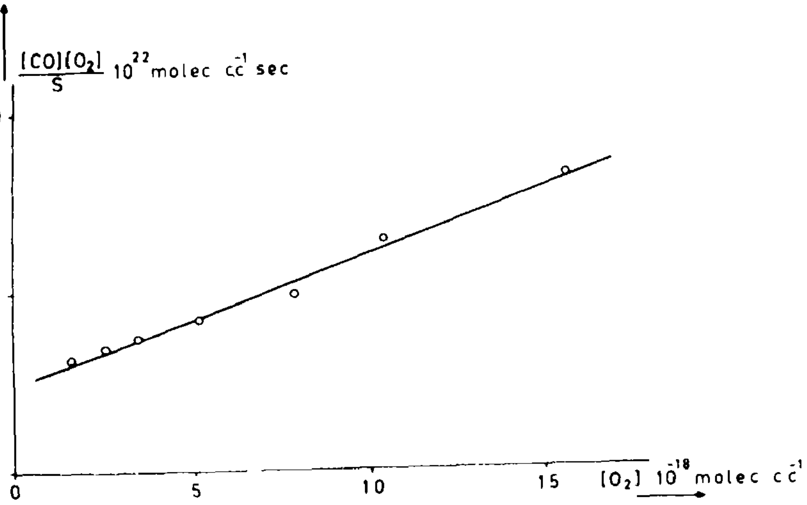


FIG. 4 Variation of the quantity $\frac{[CO][O_2]}{S}$ with O_2 concentration, at constant CO concentration, at 500 C Slope 0 37 0 02

Also a linear relation between $[CO][O_2]/S$ and [CO], and $[O_2]$ respectively, can be expected from a mechanism consisting of the bimolecular formation of an activated molecule CO_3^*, which after a certain lifetime decomposes to the original reactants CO and O_2, if not deactivated or decomposed by collision before

$$CO + O_2 \xrightarrow{k_a} CO_3^* \tag{a*}$$

$$CO_3^* \xrightarrow{k_b} CO + O_2 \tag{b*}$$

$$CO_3^* + M \xrightarrow{k_c} CO_2 + O + M \tag{c*}$$

As in the deactivation reaction (c^*) M means CO or O_2, an O atom is no ssarily a product in the reaction Assuming a stationary state for the concentrati CO_3^*, reaction (b^*) as the rate determining step leads to

$$S = \frac{k_a k_b [CO][O_2]}{k_b + k_c [M]} \qquad (h)$$

and

$$\frac{[CO][O_2]}{S} = \frac{1}{k_a} + \frac{k_c'}{k_a k_b}[CO] + \frac{k_c''}{k_a k_b}[O_2] \qquad (i)$$

Generally reaction (c^*) has a different rate constant for M = CO and M = O_2 respectively k_c' and k_c''

CONCLUSION

There is experimental evidence for the occurrence of oxygen exchange between CO and O_2, at 500 C, as a gas phase process The dependence of the exchange rate upon reactant concentrations is described by $S = k\, p_{CO}^{\,n}\, p_{O_2}^{\,m}$, wherein both n and m are smaller than unity A mechanism consistent with the experimental data is the bimolecular formation of an activated molecule, which decomposes after a certain lifetime in the original reactants, or is deactivated or decomposed by collision In this way an exchange by way of oxygen atoms is possible, but then it is necessary to assume

(a) there is a sufficiently fast formation of O atoms from O_2 at the wall of the vessel,

(b) the O atom concentration should be practically determined by the O_2 concentration,

(c) the number of O atoms per cm^3 should be considerably higher than the thermodynamic equilibrium concentration in oxygen

Alternatively a molecular mechanism ($CO + O_2 \rightarrow CO_3^*$) can also explain the experimental results On the basis of our present data it cannot be decided which of these two mechanisms is responsible for the exchange

Acknowledgements—We are grateful to Professor Dr J A A KETELAAR for helpful suggestions We thank Dr D HEYMANN for valuable discussions Mr F L MONTERIE kindly performed the mass analyses

This work is part of the research programme of the Stichting voor Fundamenteel Onderzoek der Materie (Foundation for Fundamental Research on Matter) and has been made possible by financial support from the Stichting voor Zuiver Wetenschappelijk Onderzoek (Netherlands Organisation for Pure Scientific Research)

J. Inorg. Nucl. Chem. 1963 Vol. 25 pp. 1531 to 1538. Pergamon Press Ltd. Printed in Northern Ireland

NOTES

On the third phase formation in extraction systems involving aminehydrochlorides*

(*Received* 12 *June* 1963)

THE formation of a third phase (a second organic one) is frequent in solvent extraction processes involving long-chain amines and aliphatic hydrocarbons as diluents. During an investigation of the possible composition of the third phase, its nature and behaviour, a phenomenon believed not previously reported has been observed. This phenomenon is further evidence for the prevailing assumption that third phase formation is due solely to a miscibility gap in a two-phase conjugate system.

TABLE 1.—CRITICAL INITIAL ACID CONCENTRATIONS FOR THE APPEARANCE AND DISAPPEARANCE OF THE THIRD PHASE AT 27.5

		HCl M	
Diluent	Amine	Appearance	Disappearance
Dodecane	TiOA	0.1	Upon bubbling HCl gas
	Alamine	0.1	through
	TNA	0.1	the system
Hexane	TiOA	0.1	conc. HCl
	Alamine	0.2	conc. HCl
	TNA	3.5	10
Cyclohexane	TiOA	2.9	10.5
	Alamine	7.0	9.5
	TNA	7.0	8.5

TiOA, 0.2M tri-isoOctylamine (Union Carbide)
Alamine, 0.2M Alamine 336 (General Mills)
TNA 0.2M tri-nonylamine (I.C.I.)

When solutions of tertiary amines in freshly-distilled aliphatic hydrocarbons are equilibrated with equal volumes of aqueous hydrochloric acid solutions (0.1–11.5 M) a critical initial acid concentration is expected for the formation of the third phase. This was indeed observed. It was rather unexpected, however, to observe that certain higher initial acid concentrations will cause the third phase to disappear or will prevent its formation (Tables 1 and 2). This miscibility-immiscibility of the two organic phases in equilibrium is a reversible reaction, dependent for a given diluent upon the acid and

---

* This research was supported in part by the U.S. Atomic Energy Commission Contract No. AT(30-1) 905.

to some extent, amine concentrations and the temperature. Our preliminary data* are here briefly tabulated and a tentative explanation of the phenomenon offered.

Under experimental conditions where neutralization of the amine base by the acid is complete and no excess acid is extracted the N : Cl ratio is roughly unity in both organic phases, the bulk of the amine-bearing species being in the ejected third phase. If excess acid is extracted it is essentially found in the solvent-rich phase.

Third phase formation may be understood by remembering that the dielectric property of the organic solution drastically changes with the transformation of the weakly polar amine molecule into an amine-salt ion pair having a large dipole moment. This effect is clearly exhibited by the respective solubilities. Tertiary amines, with a certain restriction due to steric factors, are completely miscible with both aromatic and aliphatic hydrocarbons, while the corresponding amine hydrochlorides have a limited solubility in aliphatic and a higher solubility in aromatic hydrocarbons and in certain derivatives of aliphatic hydrocarbons (CCl_4). The striking difference in the solvent behavior of aromatic and aliphatic hydrocarbons with equally low dielectric constants and zero dipole moments seems not to be limited to the solubility of amine salts.† The solvating power of aromatic hydrocarbons is due to a solute-solvent interaction between the benzene ring and the ammonium group of the ion-pair under consideration, thus interfering with the stabilization of the amine hydrochloride ion-pair and its subsequent aggregation.(1) This has been shown(2) to be the case for amine nitrates, which exhibit a far higher degree of aggregation in octane than in benzene. Solvent molecules in the neighborhood of the closely associated and aggregated ion pair are influenced by its electric field and consequently have a higher dielectric constant than that of the bulk solvent. Increased differences in the dielectric constants will finally lead to splitting of the organic phase.(3) The phenomenon of disappearance of the third phase can be explained by similar reasoning, an increased transfer of hydrochloric acid(4) into the non-polar diluent increasing the dielectric constant of the bulk solvent, thus diminishing the differences and enabling the phases to mix.

TABLE 2.—CRITICAL ACID CONCENTRATIONS FOR VARYING CONCENTRATIONS OF TNA IN HEXANE

TNA, M	HCl, M Appearance	HCl, M Disappearance
0.05	3.7	10
0.1	3.4	10
0.2	3.5	10
0.4	5	10
0.6	6	10
0.8	7	10

The differences in the solubilities of amine hydrochlorides in aromatic and aliphatic hydrocarbons, apparently unrelated to such physical parameters as dielectric constant and dipole moment, can be qualitatively correlated by Hildebrand's solubility parameter concept(5) On evaluating the solubility parameter δ_2 for these tertiary amines(6) we found that $\Delta\delta = (\delta_1 - \delta_2)$ has a value of 0 3–1 2 for non-polar aliphatic hydrocarbons and 1 6 2 2 for non-polar aromatic hydrocarbons and non-polar aliphatic hydrocarbon derivatives, in line with previous conclusions concerning similar phenomena in systems involving tributyl phosphate(7) This concept fails however to explain the differences observed between various aliphatic hydrocarbons, in that the initial acid concentration at which the third phase is formed increases, and that of its disappearance decreases in the order dodecane hexane, cyclohexane Calculations based upon the molar polarizability values of the amine-diluent mixtures show that the above sequence of diluents is not incidental Assuming the validity of Maxwell's relation for these low dielectric constant amines(8) their polarizability has been calculated by the Clausius-Mossotti equation(9) and the molar polarizability P_{12}, of the binary liquid mixtures evaluated P_{12} decreases in the above order of diluents, which have values of 61 1, 32 7 and 29 8 respectively immiscibility being favoured by a higher value of P_{12} This correlation between polarizability and miscibility supports the belief that the formation of the third phase is purely a miscibility gap phenomenon, since the addition of a few percent of a polar liquid such as a long-chain alcohol actually prevents its formation It was found for example that values of P_{12} for binary mixtures of aliphatic alcohols and hydrocarbons initially decrease with the first few percent of alcohols and show minima at values 10% w/w alcohol(10) This roughly coincides with the percentage of alcohols necessary to prevent the third phase formation in hydrocarbon diluents(11) We hope to express this dependence qunatitatively especially for P_{12} as a function of temperature, since the dielectric constant (and consequently the molar polarization) of non-polar and weakly polar liquids decreases with increasing temperature, accompanied by increased miscibitily of the phases

---

* Taken in part from the Ph.D. Thesis of Y. E. H. to be submitted to the Senate of the Hebrew University.

† Carboxylic acids and phenols are associated in aliphatic hydrocarbons far more than in benzene or carbon tetrachloride (H. A. POHL, M. E. HOBBS and P. M. GROSS, *J. Chem. Phys.* **9,** 408 (1941); F. A. PHILBRICK, *J. Amer. Chem. Soc.* **56,** 2581 (1934); L. J. BELLAMY and R. L. WILLIAMS, *Proc. Roy. Soc.* A **254,** 119 (1960).) This has been explained [M. M. DAVIS, *J. Amer. Chem. Soc.* **84,** 3623 (1962)] by a solvent effect interfering with aggregation, and due in the case of benzene to its π-electrons or to the $Cl^- - C^+$ bonds in the case of carbon tetrachloride.

(1) J. M. P. J. VERSTEGEN, *Trans. Faraday Soc.* **58,** 1878 (1962).

(2) E. HOGFELDT, B. BOLANDER and F. FREDLUND, *Proc.* 7th *Intern. Conf. Coord. Chem.*, Stockholm, June 1962.

(3) H. L. FRIEDMAN, *J. Phys. Chem.* **66,** 1595 (1962).

(4) W. F. LINKE, *Solubilities*, 4th Ed., Vol. 1, Van Nostrand, Princeton, 1958.

The polarizability concept of the phenomena of appearance and disappearance of the third phase as well as for reversibility in the miscibility-immiscibility equilibrium of the conjugate system formed by the two organic phases, is qualitatively similar to a discussion recently offered by FRIEDMAN(4) for binary systems of electrolytes in non-aqueous solvents that separate to form two liquid phases A quantitative theory would be much more difficult since the systems under consideration are actually quaternary ones If we consider the system as being composed of amine diluent acid and water, the phenomena are probably due to a salt-effect roughly comparable to that in the case of critical micelle concentration in non-regular systems(5, 12) Experiments of a different type have been designed to provide the information desired to substantiate the above salt-effect assumption

Acknowledgements—We wish to thank Dr P I LLOYD, Department of Nuclear Engineering and Prof J W IRVINE, Jr Department of Chemistry, Massachusetts Institute of Technology for helpful discussions

Department of Chemistry and
Laboratory for Nuclear Science
Massachusetts Institute of Technology
Cambridge, Mass
and
Department of Inorganic Chemistry
The Hebrew University
Jerusalem, Israel

A S KERTES
Y ELHANAN HABOUSHA

(5) J H HILDEBRAND and R L SCOTT, *Regular Solutions* Englewood Cliffs New Jersey 1962

(6) A S KERTES, Progress Report, Laboratory for Nuclear Science, Massachusetts Institute of Technology, May 1, 1963

(7) E FOA, N ROSINTAL and Y MARCUS *J Inorg Nucl Chem* **23**, 109 (1961)

(8) cf W McDOWELL and K A ALLEN *J Phys Chem* **63**, 747 (1959)

(9) G OSTER, *J Amer Chem Soc* **68**, 2036 (1946)

(10) O FUCHS and K L WOLF *Dielektrische Polarisation* Akad Verlag Leipzig 1935, C P SMYTH and W N STOOPS, *J Amer Chem Soc* **51**, 3312 (1929) J ERRERA in *The Dipole Moment and Chemical Structure*, Edited by P DEBYE, Blackie London 1931

(11) C F COLEMAN, F A KAPPELMAN and B WEAVER *Nucl Sci Eng* **8**, 507 (1960) F BARONCELLI G SCIBONA and M ZIFFERERO, *J Inorg Nucl Chem* **25**, 205 1963 I J JENKINS and A G WAIN, AERE-M537 (Oct , 1959)

(12) K SHINODA, *Bull Chem Soc Japan* **35**, 1213 (1962)

Formation of nitrosyl complexes in the reaction between platinum (II) nitro complexes and concentrated hydrochloric acid

(*Received* 3 *June* 1963)

In 1896 Miolati[1] studied the reaction between $K_2[Pt(NO_2)_4]$ and concentrated hydrochloric acid at low temperature (Ca 0°C) He described the isolation of a green product to which he gave the formula $K_2[Pt(NO_2)_4]$ HCl We have reinvestigated the nature of the green compound and we conclude that it is actually a platinum (II) nitrosyl complex having the formula $K_2[PtNO(NO_2)_3Cl_2]$ analogous to the six co-ordinated platinum (II) nitrosyl complexes obtained by Griffith, Lewis and Wilkinson[2] by the reaction between nitrosyl chloride and various four co-ordinated platinum (II) complexes Its infrared spectra in a nujol mull shows in addition to the characteristic bands of the co-ordinated nitro group[3] a strong band at about 1725 cm^{-1}, typical of the N O stretching frequency of the co-ordinated nitrosonium group (NO^+)[4] The reaction probably takes place as follows

$$[Pt(NO_2)_4]^{2-} + 2Cl^- + 2H^+ \rightarrow [PtNO(NO_2)_3Cl_2]^{2-} + H_2O$$

and is formally similar to the equilibrium

$$NO^+ + H_2O \rightleftarrows NO_2H \rightleftarrows NO_2^- + H^+$$

which is markedly displaced to the left in a strong acid medium[5] The green nitrosyl complex is moderately stable in dry air It reacts with water with evolution of NO yielding a colourless acid solution containing the ion $[Pt(NO_2)_3Cl]^{2-}$ as described by Miolati[1] Prolonged contact of the complex with concentrated hydrochloric acid leads to the formation of a yellow precipitate consisting of a mixture of the platinum (IV) chloro complexes $K_2[PtNO_2Cl_5]$ and $K_2[PtCl_6]$[6]

The complex cis $[Pt(NH_3)_2(NO_2)_2]$ also reacts with concentrated hydrochloric acid at ca 0 C yielding a green product with the formula $[PtNO(NH_3)_2NO_2Cl_2]$ (Found Pt, 51 0 N, 14 1, Cl, 19 1%, Req Pt, 51 90, N, 14 88, Cl, 18 87%) Its infrared spectra (nujol mull) has a strong band at about 1720 cm^{-1} attributable to the co-ordinated NO^+ group The complex is sparingly soluble in concentrated hydrochloric acid It reacts with water with evolution of NO and the formation of the insoluble platinum (II) complex $[Pt(NH_3)_2NO_2Cl]$ The trans isomer behaves in a similar manner (V_{st} N—O 1700 cm^{-1}) Our findings with the dinitrodiammine platinum (II) complexes confirm the early report by Koeffoed,[7] whose results, however, have been recently questioned[2]

Dep Quimica Inorganica
Facultad de Ciencias Exactas
Peru 222, Buenos Aires
Argentina

R Levitus
J Raskovan

[1] A Miolati, *Atti Linc* 5, 355 (1896)

[2] W P Griffith, J Lewis and G Wilkinson, *J Chem Soc* 775 (1961)

[3] F A Cotton, *Modern Coordination Chemistry* (Edited by J Lewis and R J Wilkins) p 370, Interscience, New York, (1960)

[4] J Lewis, R I Irving and G Wilkinson *J Inorg Nucl Chem* 7, 32 (1958)

[5] J Lewis and C C Addison, *Quart Rev* 9, 115 (1955)

[6] M Vezes, *Ann Chim Phys* 6, 29, 173 (1893)

[7] E Koffofd, Om nagle Nitroso Platinammoniakferbindelsen Akad Afh Kopenhagen (1894)

Base catalysed condensation of disilyl sulphide

(*Received* 18 *June* 1963, *in revised form* 1 *August* 1963)

It has recently been observed that condensation of trisilylamine, $(SiH_3)_3N$, occurs according to equation 1 when it is treated with small quantities of bases such as NH_3, CH_3NH_2, $(CH_3)_3N$ and LiH[1] Reaction only takes place when

$$3(SiH_3)_3N \rightarrow (SiH_3NSiH_2)_3 + 3SiH_4 \qquad (1)$$

---

[1] R Schaeffer and R Wells, unpublished observations See *Studies of Light Weight Elements* R Schaeffer *et al*, Technical Report No 2, Contract Nonr-908 (14) August, 1961 *also* F G A Stone, *Hydrogen Compounds of the Group IV Elements*, p 28 Prentice-Hall, New York (1962)

uid is present and some non-volatile materials are also formed If the reaction is stopped after short time the NH_3 can be recovered but after an extended period of time NH_3 can not be recovered nd non-volatile products are formed

It appears that base-catalysed condensation processes may actually represent a somewhat neral type of reaction in silicon chemistry Thus there is evidence to suggest that the condensation $SiH_3SiH_2N(CH_3)_2$ may be promoted by the presence of $(CH_3)_2NH$ (2) viz

$$2SiH_3SiH_2N(CH_3)_2 \rightarrow SiH_3SiH[N(CH_3)_2]_2 + Si_2H_6 \qquad (2)$$

Also at 0 small quantities of $(CH_3)_3N$ cause SiH_3SiH_2Br to liberate Si_2H_6 rapidly with the formation of volatile products which appear to consist of polybromodisilanes (3)

$$2SiH_3SiH_2Br \rightarrow Si_2H_4Br_2 + Si_2H_6 \qquad (3)$$

In an apparently related but different type of reaction a derivative of disilane eliminates a substituted monosilane to form a substituted polysilane Thus certain amines (4) and/or AgCN (4) have been found to act as catalysts in the condensation of Si_2Cl_6 or certain methylchlorodisilanes, viz

$$xCl_2CH_3SiSiCH_3Cl_2 \rightarrow CH_3Cl_2Si(SiCH_3Cl)_xCl + (x-1)CH_3SiCl_3 \qquad (4)$$

With $(CH_3)_3SiSi(CH_3)_2CN$, the presence of the basic cyanide group apparently causes the compound to condense spontaneously on heating (5) e g

$$2(CH_3)_3SiSi(CH_3)_2CN \rightarrow (CH_3)_3SiSi(CH_3)_2Si(CH_3)_2CN + (CH_3)_3SiCN \qquad (5)$$

The compound SiH_3SCF_3 has been found to react in the presence of $(CH_3)_3N$ according to equation 6 (6)

$$xSiH_3SCF_3 \rightarrow (-CF_2-S-)_x + xSiH_3F \qquad (6)$$

but the products are recovered as their adducts $SiH_3F \cdot N(CH_3)_3$ and $SCF_2 \cdot N(CH_3)_3$ The latter species which is non-volatile, is believed to be a polymeric adduct of thiocarbonyl fluoride (6) It would appear that the $(CH_3)_3N$ may be coordinated to the sulphur by means of the vacant 3d orbitals of the sulphur

Re-examination of some earlier unpublished results (7) indicates that $(SiH_3)_2S$ also undergoes an apparently analogous reaction with $(CH_3)_3N$ as well as with NH_3 Disilyl sulphide and NH_3 underwent rapid reaction at reduced temperatures to form a solid which could be easily sublimed *in vacuo* to form long colourless crystals The solid may be $(SiH_3)_2S \cdot 2NH_3$ with one NH_3 molecule coordinated to each silicon On standing at room temperature the crystals changed to a non-volatile white solid of composition corresponding to $SiH_3-S-SiH_2-S-SiH_3 \cdot 3NH_3$ Apparently the condensation reaction

$$2(SiH_3)_2S \rightarrow SiH_3-S-SiH_2-S-SiH_3 + SiH_4 \qquad (7)$$

took place and since silicon atoms and NH_3 molecules are present in the product in the same molar ratio it seems probable that one NH_3 molecule is coordinated to each silicon atom The fact that coordination of a $(CH_3)_3N$ molecule to a sulphur atom was postulated above for $SCF_2 \cdot N(CH_3)_3$ is not inconsistent with this suggestion since the Lewis acid character of the sulphur in SCF_2 might be expected to be considerably enhanced by the presence of the CF_2 grouping

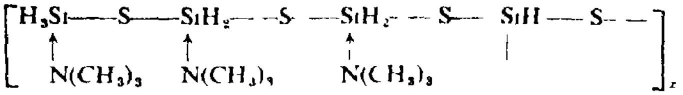
Disilyl sulphide was also found to react fairly rapidly with excess $(CH_3)_3N$ below, and at room temperature, to give a sticky, non-volatile, apparently polymeric solid of composition corresponding to $[(-SiH_2-S-) \cdot 0.75\,N(CH_3)_3]_x$ The basic reaction occurring may be represented by the equation

$$x(SiH_3)_2S \rightarrow (-SiH_2-S-)_x + xSiH_4 \qquad (8)$$

[2] M. Abedini and A G MacDiarmid, *Inorg Chem* **2**, 608 (1963)
[3] C. H Van Dyke and A G MacDiarmid unpublished results
[4] A Kaczmarczyk, M Millard and G Urry, *J Inorg Nucl Chem* **17**, 186 (1961) G D Gilbert and A R Cooper, *J Amer Chem Soc* **82**, 5042 (1960)
[5] J V Urenovitch and A G MacDiarmid, *J Amer Chem Soc* In press (1963)
[6] A J Downes and E A V Ebsworth *J Chem Soc* 3516 (1960)
[7] A G MacDiarmid, Ph D thesis Cambridge University (1955)

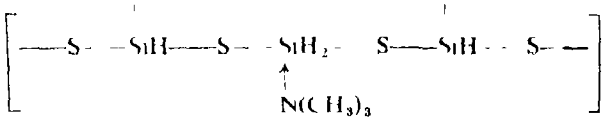
Condensation was therefore more extensive than in the case of the analogous reaction

If it were assumed that, for steric reasons, $(CH_3)_3N$ could coordinate to $-SiH_3$ and but not to $\equiv SiH$ units then the above empirical formula of the substance isolated would co exactly to the structure



$$\left[\begin{array}{ccccccccccccccc} H_3Si & - & S & - & SiH_2 & - & S & - & SiH_2 & - & S & - & SiH & - & S & - \\ \uparrow & & & & \uparrow & & & & \uparrow & & & & | & & & \\ N(CH_3)_3 & & & & N(CH_3)_3 & & & & N(CH_3)_3 & & & & & & & \end{array}\right]_x$$

On heating the product for several hours more SiH_4 and $(CH_3)_3N$ were slowly and com evolved in the molar ratio 1 2 8 The ratio is only approximate since the quantity of SiH_4 ed was very small and was not measured accurately This is qualitatively consistent with the structure decomposing to give



$$\left[\begin{array}{cccccccccc} - & S & - & \overset{|}{SiH} & - & S & - & SiH_2 & - & S & - & \overset{|}{SiH} & - & S & - \\ & & & & & & & \uparrow & & & & & & & \\ & & & & & & & N(CH_3)_3 & & & & & & & \end{array}\right]_x$$

with the liberation of SiH_4 and $(CH_3)_3N$ in the calculated ratio of 1 2 The fact that $(CH_3)_3N$ was evolved in addition to SiH_4 is added evidence to suggest that the amine is attached to silicon rather than to sulphur The solid product was not wetted or attacked by water

Experimental

Standard vacuum system techniques were employed in all operations Disilyl sulphide was synthesized as previously described(8) and was of a similar state of purity

Reaction of $(SiH_3)_2S$ *with* NH_3 $(SiH_3)_2S$(2 82 mmole) and NH_3(5 67 mmole) were sealed together in a 30 ml tube at −196 and by the time the mixture had been warmed rapidly to room temperature a white solid had formed On warming one side of the tube by the hand, long colourless crystals grew rapidly on the cooler glass surfaces The solid could at first be sublimed almost completely from one end of the tube to the other but on standing, less and less could be sublimed in this manner

After 12 hr at room temperature the reaction vessel was opened to the vacuum system and 0 2 ml of H_2 was found to be present Most of the white solid was non-volatile but even after pumping for 45 min at room temperature very small amounts of the solid slowly and continuously distilled from the reaction vessel This left a deposit of non-volatile white solid each time it was distilled in the vacuum system Silane (mol wt found, 31 9, calcd , 32 1, 1 38 mmole) was separated from excess NH_3 (mol wt found, 17 1, calcd , 17 0, 1 47 mmole) by distillation through a trap at −134° in which the latter compound condensed From the quantities of reactants consumed and SiH_4 recovered, the non-volatile white solid had the composition $(SiH_3S)_2SiH_2$ $3NH_3$ Found Si, 40 9, H, 8 30, S, 31 1, N, 20 1% Calcd for $Si_3H_{17}S_2N_3$, Si, 40 59, H,8 26, S, 30 90, N 20 25%

Reaction of $(SiH_3)_2S$ *with* $(CH_3)_3N$ $(SiH_3)_2S$ (1 24 mmole) and $(CH_3)_3N$ (2 69 mmole) were sealed together in a 15 ml tube at −196° As the tube warmed to room temperature the liquid phase became filled with a mass of small bubbles and after 45 min at room temperature it had turned to a white, fluffy, sticky solid No hydrogen was found when the tube was opened Volatile compounds were removed from the reaction tube by pumping for 1 hr After this time a very small amount of volatile material was still being slowly evolved Silane (mol wt found, 31 9, calcd , 32 1 1 21 mmole) was separated from excess $(CH_3)_3N$ (mol wt found, 59 2, calcd , 59 0, 1 73 mmole) by distillation through a trap at 134° in which the latter compound condensed From the quantities of reactants consumed and SiH_4 recovered, the non-volatile solid had the composition SiH S 0 75$(CH_3)_3N$ Found, C,25 7, Si, 26 5, H, 8 43, S, 29 6, N, 9 98% Calcd for $C_{2\ 25}Si_{1\ 00}H$ $S_{1\ 00}N_{0\ 75}$, C, 25 30, Si, 26 40, H, 8 30, S, 30 15, N, 9 85%

When the reaction vessel was surrounded with very hot water and pumped for 5 hr a small amount of volatile material was slowly and continuously evolved Distillation through a trap −134° yielded $(CH_3)_3N$ (mol wt found, 59 0, calcd , 59 0, 0 45 mmole) and SiH_4 (0 16 mmole

The white solid remaining did not melt or sublime on heating to 160° It was insoluble in ben

---

(8) H J EMELÉUS, A G MACDIARMID and A G MADDOCK, *J Inorg Nucl Chem* **1**, 194 (195

J Inorg Nucl Chem, 1963 Vol 25 pp 139 to 141 Pergamon Press Ltd Printed in Northern Ireland

BOOK REVIEWS

M STACEY, J C TATLOW and A G SHARPE **Advances in Fluorine Chemistry** 203 + vii pp, Butterworth's Publication, London, 1960 45s

It is regretted that the rough draft of this review was published in this journal instead of the following final version submitted by the reviewer

The Halogen Fluorides—Their Preparation and Uses in Organic Chemistry (W K R MUSGRAVE)

This article contains a lot of useful information which is not embraced by the volume title, i e *ADVANCES* in Fluorine Chemistry and is more properly described as a review The author could have been very much more economical in his text—terseness with clarity leads to a far more stimulating text as is readily seen if Sharpe's article is compared with Musgrave's The latter reminds me somewhat of Mellor The sections concerned with the preparations of halogen fluorides serve to give the newcomer to the field an adequate indication of the state of knowledge However, those on the uses of fluorine halides in organic chemistry are rather disappointing in that vague process details are presented where scientific results are expected

Transition Metal Fluorides and their Complexes (A G SHARPE)

Sharpe's article starts off in good style and the reader is left in no doubt as to what he is in for in the way of a chemical "treat" The article deals factually, concisely and in a very readable manner with advances in the fluoride chemistry of transition metals which have taken place in the last decade He deals adequately with theoretical aspects of the crystalline state of these complexes, preparative methods and surveys of a wide range of compounds are presented in a well organized manner This chapter provides very good reading for all students of inorganic chemistry, whether aged 18 or 80, and is a must for those with a particular interest in fluorides

Fluoroboric Acids and their Derivatives (D W A SHARP)

Like A G Sharpe's article, this one is very adequately presented Of the fluoroborates the tetrafluoroborate receives the lion's share of attention but of course this only reflects on their relative stabilities as compared with tri- and di-fluoroborates Physical constants, crystal considerations and thermodynamic properties receive their due acknowledgement Reactions, formations and descriptions of a large number of inorganic, oxonium and carbonium tetrafluoroborates are presented Again a very strong recommendation is made as to the value of this article to the general and specialized reader

The Electrochemical Process for the Synthesis of Fluoro-organic Compounds (J BURDON and J C TATLOW)

This article actually comprises more than the title suggests since some (small) consideration is also given to the synthesis of inorganic fluorocompounds Included are descriptions of apparatus, operating conditions and processes The results of the latter are presented in a much more satisfactory manner than those of the first article and the reader feels that he is getting more scientific value for his money Fluorination of a wide variety of compounds is considered Whilst admitting that the electrochemical process is still an art in many respects the authors nevertheless round off the article with a very useful discussion of possible mechanisms of this type of fluorination

Exhaustive Fluorinations of Organic Compounds with High-Valency Metallic Fluorides (M STACEY and J C TATLOW)

The type of fluorination described here is probably familiar to the general reader most of whom will be aware, for instance, of the fluorinating potentialities of CoF_3 Whilst descriptions of apparatus and procedure etc are in general satisfactory it is surprising to find such an uninformative photograph (p 171) included a line diagram with scale tells much more Fluorinations with CoF_3, AgF_2, MnF_3, CeF_4 and PbF_4 are described and a brief mention is made of others e g UF_6 (the lower valency fluoride which is usually the by-product is here the main product) Again a useful discussion of possible mechanisms is included

F S MARTIN

cyclohexane and carbon disulphide but it appeared to react with dry acetone. It was not wetted by water and water did not appear to react with it. However, it was decomposed rapidly by aqueous KOH with liberation of H_2 and $(CH_3)_3N$.

Acknowledgment—The author wishes to express his thanks to Professor H. J. Emeléus for advice and many helpful discussions during the period in which this research was being carried out.

A. G. MacDiarmid

John Harrison Laboratory of Chemistry
University of Pennsylvania
Philadelphia 4
Pennsylvania, U.S.A.

Acid–base equilibrium constants in fused KNO_3

(*Received* 31 *July* 1963)

Despite the increasing interest in the field of molten salts, practically nothing has been reported concerning acid base equilibrium constants in the melts. Lux[(1)] defines acids and bases in fused salts as

$$\text{Acid} + O^{2-} \rightleftharpoons \text{Base}$$

The measurement of the oxygen ion activity may be regarded, therefore, as an estimation of acid base equilibria in melts. Variations in the oxide ion activity in a melt could be followed by measuring the potential of either an oxygen electrode[(2-8)] or a metal-metal oxide electrode[(7, 9-11)] relative to a suitable electrode.

The present authors have recently developed the technique for potentiometric acid base titrations in molten salts.[(12-16)] An oxygen (Pt) electrode was used as indicator electrode and at the equivalence points, sharp potential drops were recorded which corresponded to the amounts of the acids in the melts. The determination of single acid base equilibrium constants was, however, hampered because of the irreversible behaviour of the oxygen electrode in unbuffered melts.[(16)] The potential of this electrode varied linearly with the logarithm of the oxygen ion concentration (activity) but the slope of the E – log[O^{2-}] curve amounted to 2.303[$(RT)/F$] rather than 2.303 [$(RT)/(2F)$] theoretically expected for the oxygen electrode. The exact $E°$ value for the oxygen electrode could not, therefore, be established.

[(1)] H. Lux, *Z. Elektrochem.* **45**, 303 (1939).

[(2)] E. Baur and H. Ehrenberg, *Z. Elektrochem.* **18**, 1002 (1912); E. Baur, W. D. Treadwell and G. Trumpler, *Z. Elektrochem.* **27**, 199 (1921); E. Baur and R. Brunner, *Z. Elektrochem.* **41**, 794 (1935).

[(3)] H. Lux, *Z. Elektrochem.* **52**, 220, 224 (1948).

[(4)] P. Czaki and A. Dietzel, *Glastech. Ber.* **18**, 33, 65 (1940).

[(5)] B. A. Rose, G. J. Davis and H. J. T. Ellingham, *Faraday Soc. Dis.* **4**, 154 (1948).

[(6)] H. Flood, T. Forland and K. Motzfeld, *Acta Chem. Scand.* **6**, 257 (1952).

[(7)] G. J. Janz and Saegusa, *Electrochim. Acta* **7**, 393 (1962).

[(8)] D. G. Hill, B. Porter and A. S. Gillespie, *J. Electrochem. Soc.* **105**, 408 (1958).

[(9)] S. M. Selis, G. R. B. Elliott and L. P. McGinnis, *J. Electrochem. Soc.* **106**, 134 (1959).

[(10)] H. A. Laitinen and B. B. Bhatia, *J. Electrochem. Soc.* **107**, 705 (1960).

[(11)] M. Rolin and J. J. Gallay, *Electrochim. Acta* **7**, 153 (1962).

[(12)] A. M. Shams El Din, *Electrochim. Acta* **7**, 285 (1962).

[(13)] A. M. Shams El Din and A. A. A. Gerges, *J. Electroanalyt. Chem.* **4**, 309 (1962).

[(14)] A. M. Shams El Din and A. A. A. Gerges, *Electrochim. Acta*. In press.

[(15)] A. M. Shams El Din, A. A. El Hosary and A. A. A. Gerges, *J. Electroanalyt. Chem.* In press.

[(16)] A. M. Shams El Din and A. A. A. Gerges, *Proc. 1st Austral. Conf. Electrochem.* Pergamon Press. In press.

We have now found that the Cu/CuO electrode in molten KNO_3 at 350°C varied its potential linearly with the logarithm of the oxide ion concentration The slope of the $E - \log[O^{2-}]$ curve amounts to 2.303 [(*RT*)/(2*F*)] at the working temperature The *E* value for the $Cu/CuO/O^{2-}$ half cell was calculated to be −830 mV relative to a Ag/Ag(I) reference electrode The Cu/CuO electrode was used as an indicator electrode in the titration of the acid $K_2Cr_2O_7$ with Na_2O_2 in fused KNO_3 The equilibrium constant of the reaction

$$Cr_2O_7^{2-} + O^{2-} \rightleftharpoons 2CrO_4^{2-},$$

viz ,

$$K = \frac{[CrO_4^{2-}]^2}{[Cr_2O_7^{2-}][O^{2-}]},$$

was computed to be 1.8×10^{13}

With the help of the standard $Cu/CuO/O^{2-}$ potential in molten KNO_3, the normal O O potential in the same melt was theoretically calculated This last value viz , 796.7 mV was used to compute the equilibrium constant of a number of acid base reactions The results obtained were as follows

$2PO_3^-$	O^{2-}	$P_2O_7^{4-}$,		$K = 3.1 \times 10^{15}$
$2H_2PO_4^-$	$+ O^{2-}$	$2HPO_4^{2-}$	H_2O,	$K = 3.9 \times 10^{13}$
$V_2O_7^{4-}$	$+ O^{2-}$	$2VO_4^{3-}$		$K = 4.5 \times 10^{8}$
$P_2O_7^{4-}$	O^{2-}	$2PO_4^{3-}$		$K = 6.6 \times 10^{2}$
$2HPO_4^{2-}$	O^{2-}	$2PO_4^{3-}$	H_2O	$K = 2.8 \times 10^{3}$
$2HAsO_4^{2-}$	$+ O^{2-}$	$2AsO_4^{3-}$	H_2O,	$K = 2.6 \times 10^{2}$

Details of the measurements and extended discussion of the results will be published later

Acknowledgement—The junior author is grateful to the National Research Center for the award of a research fellowship

A M SHAMS EL DIN
A A A GERGIS

Laboratory of Electrochemistry and Corrosion
National Research Centre
Dokki
Cairo, U A R

38975
Cal 25.4.82

P A I WHITE and S L SMITH **Inert Atmospheres** 235 pp Butterworths, London, 1960 50s

THE PROGRESS of the Atomic Energy Industry during the past decade has produced a remarkable development of the techniques available for the safe handling of reactive and pyrophoric materials Up to the present time the principal beneficiary has been the Industry which stimulated this development However it is inevitable that these techniques will find wider applications since many operations can be performed in inert atmospheres at less cost and with greater ease than they can in a vacuum

This development has resulted from the extensive use of inert gases to provide atmospheres in which research development and production work on uranium, plutonium and beryllium could be carried out The authors who have been responsible for the direction of these activities at the Atomic Weapons Research Establishment at Aldermaston have written this book with the benefit of their extensive experience It will be helpful to all who are concerned with work in inert atmospheres from the research worker to the plant designer or maintenance engineer

The first five chapters deal with the principles of inert gas systems, the purification of atmospheres by chemical and physical methods and with the application of purification processes to meet the specific demands of a work-space handling a particular material The remainder of the book deals comprehensively with the cost design and operational aspects of inert gas work-spaces and purification plants

The most widely used inert gas in the United Kingdom is argon which is available relatively cheaply in a state of high purity Helium is generally more expensive and more difficult to pump but has advantages over argon as a potential coolant for nuclear reactors since it combines freedom from neutron irradiation induced radioactivity with excellent heat transfer characteristics

The Chapter on leak tightness and testing is a most valuable one which contains a full description of sources of atmosphere contamination and methods for assessing the integrity of the work-space The capacity and design of the purification plant depends almost entirely on the desired purity of the working atmosphere and the rate at which this is contaminated by impurities from the atmosphere surrounding the work-space

The use of steel for work-space enclosures is certainly to be recommended except where there is a large concentration of corrosive vapour within the relatively stagnant inert atmosphere However in the reviewer's opinion it is neither necessary nor desirable to reduce viewing areas to a minimum consistent with the flexibility and ease of operation desired and simplicity of seal design" Where pyrophoric or radioactive materials are being handled cuts or tears in gloves which result from groping into blind areas of a box may lead to fires or spreads of radioactivity In cases where viewing areas have been expanded to the maximum, consistent with the maintenance of box stability, the resultant increase in the concentration of impurities in the box atmosphere has been almost insignificant

Although the amount of work being carried out in inert atmosphere work-spaces is increasing rapidly the problems implicit in such work are by no means all solved In particular improved methods for measuring impurity concentrations below 50 vpm and for preventing or controlling explosions and fires are needed

This book, which is the first one to deal with this broad subject, will be an invaluable guide to newcomers to the field and a useful reference for experienced workers

L E RUSSELL

M C DAY, Jr and J SELBIN *Theoretical Inorganic Chemistry* xiv 413 pp Reinhold, New York, 1962 96s

THIS BOOK deserves a warm welcome Although intended primarily as a students' textbook, it should prove of value to a much wider circle of readers

Chapters 1 6 and 9 deal with valency and structural problems, starting from the fundamentals of the quantum theory and of wave mechanics, proceeding to the periodic table and the nature of chemical bonds, and going on to inorganic stereochemistry and co-ordination chemistry These chapters are excellent They present the argument with admirable clarity, making it perfectly plain at each step just what is being done and why The authors have presumably thought through all the numerous difficulties raised by their students in the course of their teaching, and the result is a most readable and comprehensible text, even when it is most mathematical Furthermore, these chapters cover all the essential ground up to quite an advanced level, and deal for example with such modern topics as crystal field theory

It should perhaps be mentioned that no attempt is made to deal systematically with crystal structure, though there are naturally many passing references to the subject.

Three of the remaining chapters in the book are concerned with aspects of solution chemistry, while the last chapter is entitled "Theory of the Nucleus." The same high standard of presentation is maintained, and the treatment is thoroughly sound, but the choice of subject-matter is open to some criticism. In the limited space allocated, it is impossible to treat either solution chemistry or radiochemistry in the comprehensive fashion of the chapters on valency questions. Useful reading material is provided, but the degree student will have to look elsewhere for his main texts. Some prospective purchasers may indeed feel that they would have preferred to avoid the additional expense of buying chapters 7, 8, 10 and 11.

Be that as it may, the book should enable many chemists to bring up to-date their knowledge of the theory underlying inorganic chemistry.

H. A. C. McKay

Borax to Boranes (Advances in Chemistry Series no. 32). Edited by R. F. Gould. pp. viii + 244. American Chemical Society, Washington D.C. 1961. $5.00.

This book, in a pleasant paper-back format, consists mainly of a collection of papers that were presented at a symposium called "Borax to Boranes." It formed part of an ACS meeting in 1958, and was to have been published afterwards with the late Professor G. W. Schaeffer as editor; it now appears, together with three extra papers presented at Boston in 1959, dedicated to the memory of this most active worker in the field.

The first reaction is one of disappointment that so long has elapsed before the book has become generally available. A closer survey, however, shows that it is not quite so behind the times: there are many references to work published in 1959 and some even more recent. Clearly some of the papers have been brought up-to-date since their presentation.

There are several quite clearly defined sections to the book, although the papers are not grouped together entirely in such a way. After a brief introduction and an intriguing biographical account of some of the pioneers in this field comes a group of five papers on boron itself and some of its inert compounds and minerals. Then follows the largest group of nine papers chiefly concerned with the boranes: their preparation, interconversion, pyrolysis, alkylation and oxidation. Two papers on mass spectrometry and infrared absorption deal mainly with boranes and might be included in this group. Metal derivatives of the boranes are then discussed in two papers, and their formulation as salts is examined. Three more contributions follow on boron-nitrogen compounds: one is concerned with the crystal structure of ammonia adducts of B_4H_{10} and BH_2Cl, another gives a valuable summary of borazine chemistry, while the third describes studies directed towards polymer formation. The boroxines, organoboron compounds, and a survey of the field from a chemical engineering standpoint comprise the subjects of the last four papers.

The book naturally suffers from the inherent defects of a compilation of this kind: there is a good deal of overlapping, there are wide gaps, and the standard of the papers is variable. A newcomer to the field might find it confusing. But those already familiar with boron chemistry will find here much of interest and much that will stimulate. Thanks to the lure of high-energy fuels some of the most fascinating inorganic chemistry of our time has been discovered and is reported here.

B. J. Aylett

ERRATA

W. *JOHN and E. J. LOMBARD The occurrence of delayed-neutron precursors. J. Inorg. Nucl. Chem.* **11**, *81–83 (1959). Page 83 Table 2 column 1, lines 9, 10, 11 and*

For [illegible]Sb, [illegible]I, [illegible]Cs *and* [illegible]La

read [illegible]Sb, [illegible]I, [illegible]Cs *and* [illegible]La

D. M. GRANT and R. KOLLRACK Absorption spectra and configuration of the ammine complexes of copper(II). *J. Inorg. Nucl. Chem.* **23**, 25–29 (1961).

DURING the preparation of our manuscript it was decided for the sake of completeness that Table 2 should be enlarged to contain the values for the mono- and triammine compounds although these values were not essential to the tenor of the paper. In doing so an unintentional error in transcription was made in the values reported by BJERRUM, BALLHAUSEN and JORGENSEN [*Acta Chem. Scand.* **8**, 1275 (1954)] for these latter two complexes. While this oversight does not in any way affect our conclusions, we would like to extend our utmost apology to Professor Bjerrum and his associates for this error. The correct values are given in the following table along with the theoretical ones proposed by the two sets of authors to eliminate any confusion resulting from the mistaken entries.

Experimental and calculated maxima of principle absorption peak given in mμ for the ammine complexes of copper(II)

Copper(II) Ion	GRANT and KOLLRACK		BJERRUM *et al.*	
	Exp	Calc	Exp	Calc
Tetraaquo	800		790	
Monoammine	752	—	745	710
Diammine	678	674(trans)	680	670(cis)
			~600(shoulder)	620(trans)
Triammine	621		645	660
Tetraamine	581		590	-
Pentaammine			640	

University of Utah
Salt Lake City, Utah

DAVID M. GRANT

J. Inorg Nucl Chem 1963 Vol 25 pp 143 to 164 Pergamon Press Ltd Printed in Northern Ireland

ALPHA HALF-LIVES OF ^{216}Po, ^{217}At AND ^{218}Rn*

H DIAMOND and J E GINDLER
Argonne National Laboratory, Argonne, Illinois

(*Received 5 June* 1962, *in revised form* 17 *July* 1962)

Abstract—The α-half-lives of ^{216}Po, ^{217}At and ^{218}Rn have been measured to be 0.145 ± 0.002 sec, 0.0323 ± 0.0004 sec and 0.035 ± 0.001 sec, respectively The alpha hindrance factor of ^{217}At has been calculated to be 1.2 on the basis of its measured half-life and an α-particle energy of 7.064 MeV

FROM simple barrier-penetration theory of α-decay, one would expect the logarithm of the α-half-life to be proportional to the reciprocal of the square-root of the alpha decay energy[1,2], i e,

$$\log_{10} t_{1/2} = A_z Q^{-1/2} + B_z \tag{1}$$

Such a relation can be demonstrated for even–even isotopes of even Z elements if $t_{1/2}$ is the partial ground-state α-half-life and Q is the effective total decay energy That is, Q equals the sum of the α-particle energy, recoil energy and an orbital electron screening correction The constants A_z and B_z are dependent upon the atomic number of the element They may be determined by a least-squares fit of the data to Equation (1)

Odd-nucleon α-emitters in general, are not represented by the theory expressed in Equation (1) Deviations from theory may be expressed in terms of a hindrance factor, F[1,2]

$$\log_{10} F = \log_{10} t_{1/2} - A_z Q^{-1/2} - B_z, \tag{2}$$

where $t_{1/2}$ is an α group's partial half-life For odd Z elements the values of A_z and B_z are taken as the arithmetical mean of the corresponding values of the two neighbouring even Z elements

In most cases of odd-nucleon α-emission, it is observed that F is greater than one That is, odd-nucleon alpha decay proceeds more slowly than the ground-state transitions of neighbouring even-even nuclides Astatine-217, however, whose half-life has been reported to be 0.018 sec,[3,4] would have a hindrance factor of 0.6[1,2] The α-particle energy of this nuclide has recently been measured as 7.064 MeV[5] Therefore, to determine whether the abnormally fast decay rate of ^{217}At is a real phenomenon or not, the half-life of this nuclide was measured

Similarly, ^{218}Rn, an even even nuclide having a half-life of 0.019 second[6] and an α-particle energy of 7.127 MeV,[7] does not give the proper relation (Equation 1) with

---

* Based on work performed under the auspices of the U S Atomic Energy Commission

[1] C J GALLAGHER, Jr and J O RASMUSSEN, *J Inorg Nucl Chem* **3** 333 (1957)

[2] I PERLMAN and J O RASMUSSEN, *Alpha Radioactivity*, Vol 42, *Handbuch der Physik* Springer-Verlag, Berlin (1957)

[3] F HAGEMANN L I KATZIN, M H STUDIER, A GHIORSO and G T SEABORG *Phys Rev* **72**, 252 (1947)

[4] F HAGEMANN, L I KATZIN, M H STUDIER, G T SEABORG and A GHIORSO *Phys Rev* **79**, 435 (1950)

[5] A A VOROB'EV, A P KOMAR and V A KORALEV, *Zh Eksptl' i Teoret Fiz* **39**, 70 (1960) *Soviet Phys JETP* **12**, 50 (1961)

[6] M H STUDIER and E K HYDE, *Phys Rev* **74**, 591 (1948)

[7] F ASARO and I PERLMAN, *Phys Rev* **104**, 91 (1956)

the reported half-lives [illegible] particle energies of ^{220}Rn and ^{222}Rn.[1,2] It was [illegible] decided [illegible] this nuclide. A more recent measurement [illegible] of the ^{218}Rn half-life [illegible] came to the attention of the authors after [illegible] work was [illegible] together with a 7.127 MeV α-particle energy [illegible] defined by Equation (1).

The [illegible] was measured as 0.145 ± 0.015 second[9] and [illegible] 0.008 second [illegible] of this nuclide is in the millisecond range and its measured [illegible] particle energy of 6.775 MeV[11] are [illegible] with the half-life [illegible] half-life was measured [illegible] the performance of [illegible]

EXPERIMENTAL

Preparation of samples [illegible] radioactive series that contains [illegible] *Each of the nuclides studied* [illegible] longer lived predecessors were [illegible] *was kept small (60 to 600 counts/min) to min*[illegible] *described* [illegible] *Polonium-216 was* [illegible] *the radioactive decay of* [illegible] *Th.**

$$^{228}\text{Th} \xrightarrow[1.910\ \text{yr}]{5.42\ \text{MeV}\ \alpha} {}^{224}\text{Ra} \xrightarrow[3.64\ \text{days}]{5.68\ \text{MeV}\ \alpha} {}^{220}\text{Rn} \xrightarrow[51.5\ \text{sec}]{6.28\ \text{MeV}\ \alpha}$$

$$^{216}\text{Po} \xrightarrow[0.158\ \text{sec}]{6.77\ \text{MeV}\ \alpha} {}^{212}\text{Pb} \xrightarrow[10.64\ \text{hr}]{\beta} {}^{212}\text{Bi} \xrightarrow[60.5\ \text{min}]{\beta} {}^{212}\text{Po} \xrightarrow[3.04\times 10^{-7}\ \text{sec}]{8.780\ \text{MeV}\ \alpha} {}^{208}\text{Pb}$$

$$^{212}\text{Bi} \xrightarrow[60.5\ \text{min}]{6.047\ \text{MeV}\ \alpha} {}^{208}\text{Tl} \xrightarrow[3.10\ \text{min}]{\beta} {}^{208}\text{Pb}$$

Two ^{217}At-containing samples were prepared. Sample ^{217}At-1 was a deposit of ^{229}Th and equilibrium products.[12]

$$^{229}\text{Th} \xrightarrow[7340\ \text{y}]{4.85\ \text{MeV}\ \alpha} {}^{225}\text{Ra} \xrightarrow[14.8\ \text{days}]{\beta} {}^{225}\text{Ac} \xrightarrow[10.0\ \text{days}]{5.818\ \text{MeV}\ \alpha} {}^{221}\text{Fr} \xrightarrow[4.8\ \text{min}]{6.33\ \text{MeV}\ \alpha}$$

$$^{217}\text{At} \xrightarrow[?]{7.064\ \text{MeV}\ \alpha} {}^{213}\text{Bi} \xrightarrow[47\ \text{min}]{\beta} {}^{213}\text{Po} \xrightarrow[4.2\times 10^{-6}\ \text{sec}]{8.35\ \text{MeV}\ \alpha} {}^{209}\text{Pb} \xrightarrow[3.30\ \text{hr}]{\beta} {}^{209}\text{Bi}$$

Sample ^{217}At-2 was prepared by collecting recoil atoms from the α-decay of ^{229}Th. After several weeks of decay, this sample contained only the alpha activities of ^{225}Ac and its daughter products.

Radon-218 is a member of the artificially-prepared protactinium[6] series.[12]

$$^{230}\text{Pa} \xrightarrow[17.7\ \text{days}]{} {}^{230}\text{U} \xrightarrow[20.8\ \text{days}]{5.884\ \text{MeV}\ \alpha} {}^{226}\text{Th} \xrightarrow[30.9\ \text{min}]{6.33\ \text{MeV}\ \alpha} {}^{222}\text{Ra} \xrightarrow[38\ \text{sec}]{6.55\ \text{MeV}\ \alpha}$$

$$^{218}\text{Rn} \xrightarrow[?]{6.813\ \text{MeV}\ \alpha} {}^{214}\text{Po} \xrightarrow[1.64\times 10^{-4}\ \text{sec}]{7.680\ \text{MeV}\ \alpha} {}^{210}\text{Pb} \xrightarrow[19.4\ \text{years}]{\beta} {}^{210}\text{Bi} \xrightarrow[5.013\ \text{days}]{\beta}$$

$$^{210}\text{Po} \xrightarrow[138.4\ \text{days}]{5.305\ \text{MeV}\ \alpha} {}^{206}\text{Pb}$$

Protactinium-230 was prepared by bombarding a metallic thorium target with 20-MeV deuterons. After allowing the induced activities to decay several days, the thorium target was dissolved in concentrated hydrochloric acid. The uranium fraction, formed by the decay of protactinium isotopes, was isolated by means of an anion exchange column using various concentrations of HCl as eluting agents. As a final purification, the uranium was extracted as the nitrate with diethyl ether and then back-extracted into water. A portion of this solution was used as the ^{218}Rn-containing sample. The deposit contained only five α-emitting nuclides in equilibrium. The ^{210}Po α-group was not detected because of the hold-up at 19.4 years ^{210}Pb. The deposit also contained ^{232}U formed by the decay of ^{232}Pa. At time of measurement, the amount of ^{232}U α-activity was slightly in excess of the ^{230}U activity However, no daughter activities of ^{232}U were detected

---

* Half-life and α-particle energy values, unless otherwise noted, have been taken from STROMINGER, HOLLANDER and SEABORG.[12] The energy of the most abundant α-group is given.

[8] C. P. RUIZ, Thesis, University of California, UCRL-9511, (1961). Unpublished.

[9] H. G. J. MOSELEY and K. FAJANS, *Phil. Mag.* **22**, 629 (1911).

[10] A. G. WARD, *Proc. Roy. Soc.* **181**, 183 (1942).

[11] G. H. BRIGGS, *Rev. Mod. Phys.* **26**, 1 (1954).

[12] D. STROMINGER, J. M. HOLLANDER and G. T. SEABORG, *Rev. Mod. Phys.* **30**, 585 (1958).

Electronics

Fig 1 represents a block diagram of the equipment used in the experiment α-particles were detected in a silicon surface barrier particle detector biased at 45 V The geometry was approximately 40 per cent of 4π Pulses from α-particles were amplified through pre-amplifier and linear amplifier circuits and sent to two single-channel pulse analysers These analysers were operated differentially The first analyser emitted a signal each time it received a pulse corresponding to the α-decay energy of the immediate parent of the nuclide under investigation, i e, pulses from alpha decay of ^{220}Rn, ^{221}Fr and ^{222}Ra for the nuclides ^{216}Po, ^{217}At and ^{218}Rn, respectively The emission of such a pulse triggered the sweep of a 400-channel analyser operating in the time-analysis (multiscaler) mode In this mode of operation, each of the 200 or 400 channels used was successively opened and closed to incoming signals from the second single-channel pulse analyser After each channel had been opened and closed in turn, the 400-channel analyser remained off until another pulse from the first single-channel analyser initiated a new sweep Any pulse from the first single-channel analyser occurring during a sweep was ignored

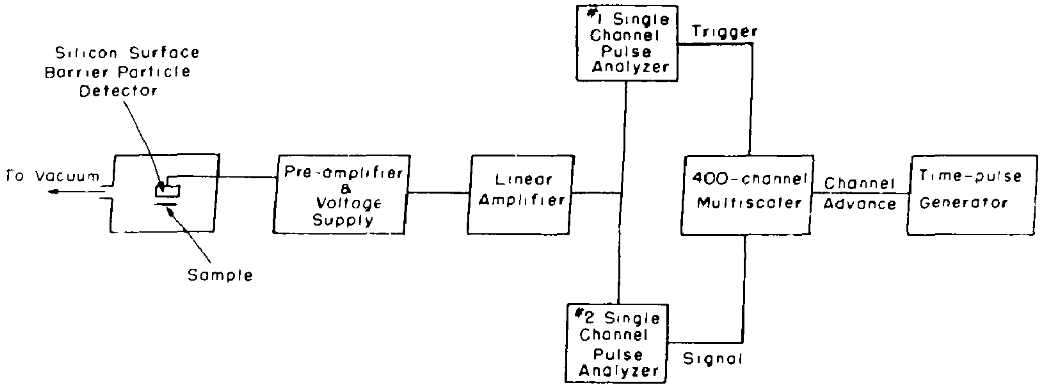

#1 Single Channel Pulse Analyzer
Trigger
Silicon Surface Barrier Particle Detector
To Vacuum
Pre-amplifier & Voltage Supply
Linear Amplifier
400-channel Multiscaler
Channel Advance
Time-pulse Generator
Sample
#2 Single Channel Pulse Analyzer
Signal

FIG 1 Block diagram of the apparatus Analyser #1 responds only to the α-decay of a parent nuclide (^{220}Rn ^{221}Fr or ^{222}Ra) which initiates the time-sweep of the multiscaler Analyser #2 responds only to the α-decay of the nuclide being studied (^{216}Po, ^{217}At or ^{218}Rn) and enters a count in whichever multiscaler channel is open at the time

The second single-channel analyser emitted a signal whenever it received a pulse from the α-decay of a nuclide under investigation (^{216}Po, ^{217}At or ^{218}Rn) This signal was then recorded in the particular channel of the multiscaler open at that time

The length of time that each channel remained open and consequently the time required to sweep all channels was determined by one of three types of external time-pulse generators Sixty cycle alternating current line frequency was used to drive a mercury relay that gave pulses of 16⅔ msec separation Pulses of 1 msec separation were generated by a 1000 c/s oscillator whose frequency was stabilized by a tuning fork Similarly, a 1000 kc/s oscillator stabilized by a quartz crystal was used to obtain pulses separated by one and ten milliseconds The frequency of the latter oscillator was reduced by means of decade scalers to produce pulses of the proper frequency

The agreement between half-lives measured by the three methods of time-pulse generation served as a useful calibration of each method Other tests were made, however to check the accuracy of time-measurement

(1) The mean pulse-rate of each time-pulse generator was verified by counting its output pulses in a multipurpose counter for a period of 10 min An ordinary electric timer was used to measure the counting time

(2) The equal time-spacing of the multiscaler channels was roughly shown in the following manner The time-sweep of the multiscaler was initiated by the signal from a 60 c/s pulse generator Pulses from α-particles of a 10^6 counts/min americium curium source were sent to the second single-channel pulse analyser This analyser was operated as an integral counter with essentially zero bias to α-particle pulses Since the radioactive nuclei in the α-source decay in a statistically random manner, one would expect the number of counts in channels of equal time-spacing to vary randomly about some average number This also, was the observed case

Several checks of this type showed the randomness of the count to be caused by counting statistics rather than by a distribution of channel time-spacings about some average spacing.

RESULTS AND DISCUSSION

Data collected in the manner just described are characteristic of those collected for a two-component decay curve. The first component arises from the radioactive decay of the nuclide under investigation.(13) The second represents a background of chance events. These events occur whenever a nuclide being studied decays during a multiscaler time-sweep that has been initiated by some parent nuclide other than its own. Such events should occur at random and should be independent of the time between the start of the time-sweep and the entry of the count.

A curve of this type may be represented mathematically by the expression,

$$N(t) = Ce^{-\lambda t} + D, \qquad (3)$$

where $N(t)$ is the number of decay events observed at time t, C is a constant equal to the number of true decay events of the nuclide under investigation at $t = 0$, D is a constant representing the number of chance events and λ is the decay constant, $(\log_e 2)/t_{1/2}$, of the nuclide being studied.

Data collected for the decay of ^{216}Po, ^{217}At and ^{218}Rn are shown, respectively, in Figs. 2, 3 and 4. Smooth curves have been drawn through the data. These curves have been derived by a computer programme(14) which involves a minimized chi-squared

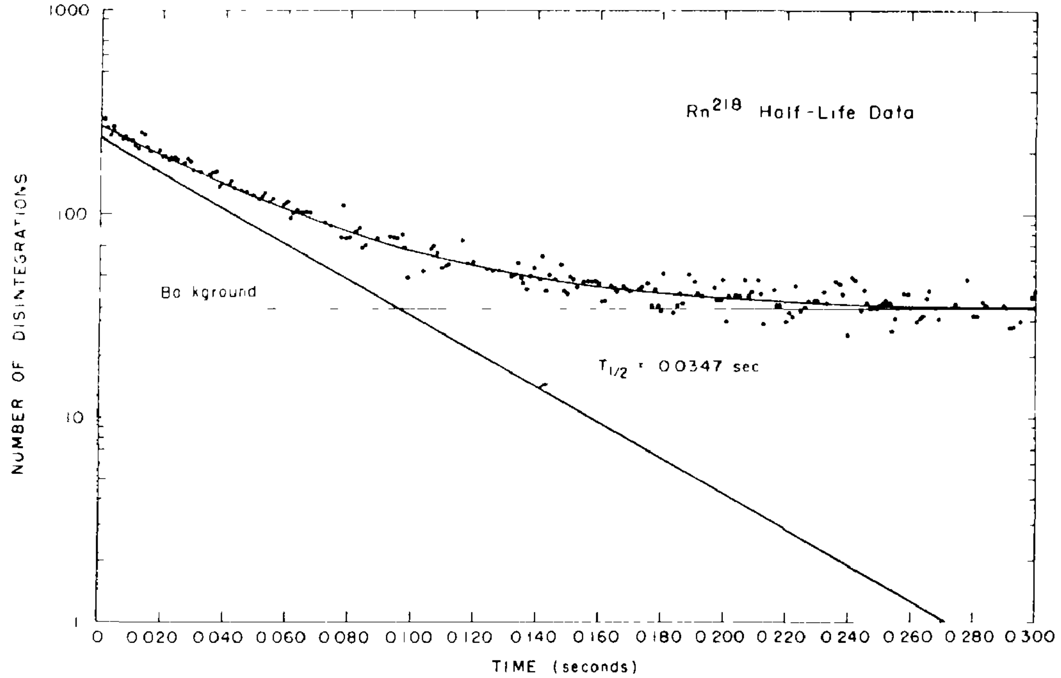


FIG. 2 — Decay curve for ^{216}Po. Zero time was determined by the γ-decay of ^{220}Rn. A quartz crystal oscillator was used as the time-pulse generator.

---

(13) E. V. SCHWEIDLER, *Congrès Internat. Radiologie, Liège* (1905). See also, for example, G. FRIEDLANDER and J. W. KENNEDY, *Introduction to Nuclear and Radiochemistry*, p. 6. J. Wiley, New York (1955).

(14) W. C. DAVIDON, Argonne National Lab. Report, ANL-5990, 1959. Unpublished. The procedure in this report was adapted to analyse a sum of exponential terms with an IBM-704 computer by K. E. HILLSTROM and B. S. GARBOW. Private communication.

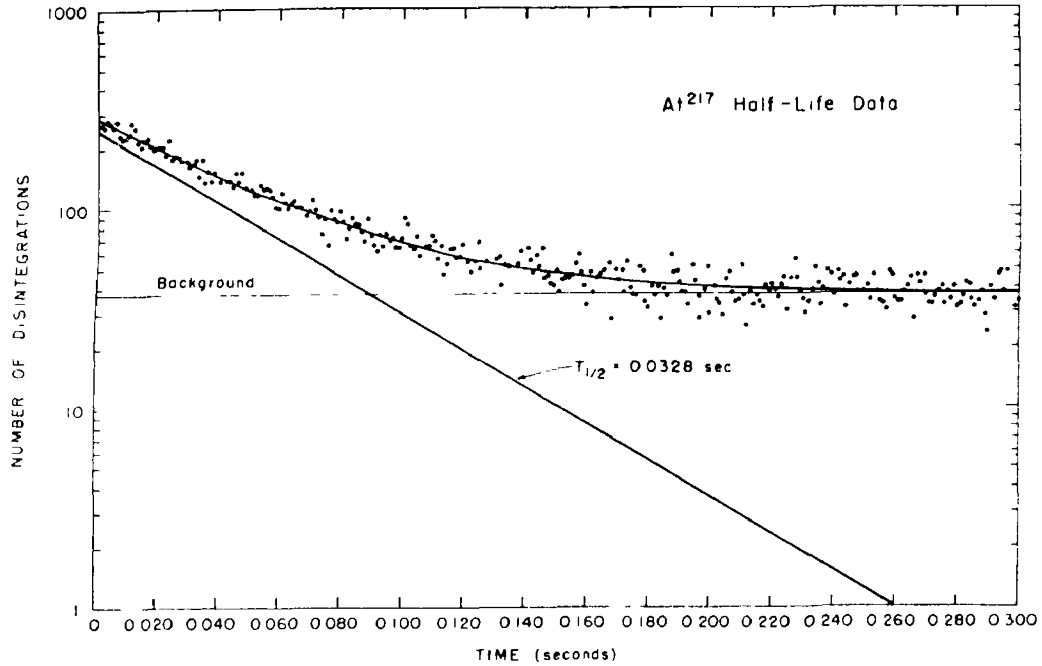


FIG. 3.—Decay curve for ^{217}At. Zero time was determined by the alpha decay of ^{221}Fr. A quartz crystal oscillator was used as the time-pulse generator.

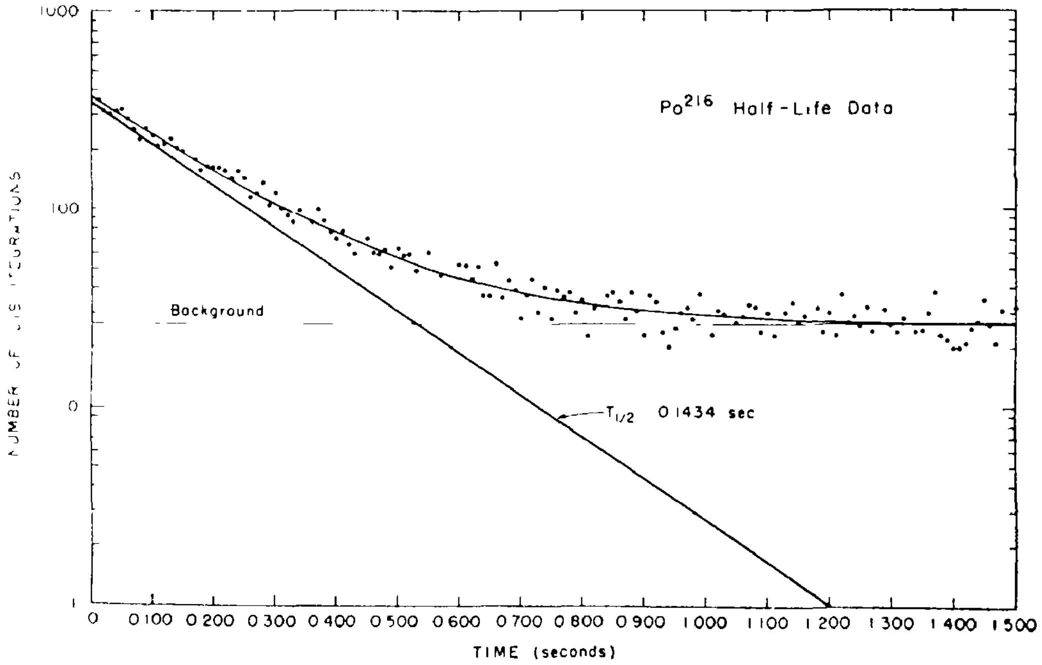


FIG. 4.—Decay curve for ^{218}Rn. Zero time was determined by the α-decay of ^{222}Ra. A quartz crystal oscillator was used as the time-pulse generator.

sum fit of the data to Equation (3). Values of the half-lives, $(\log_e 2)/\lambda$, and backgrounds D, calculated from such fits of the data are also shown in the figures.

The chi-squared sum analyses indicated that it was not unwarranted to assume that the data could be represented by Equation (3). The chi-squared test showed further that the only important source of random error was the fluctuations inherent in nuclear decay.

TABLE 1. NUCLEAR HALF-LIVES DETERMINED FOR ^{216}Po, ^{217}At AND ^{218}Rn

Nuclide Sample	Method of time pulse generation	Half-life (sec)	Standard error (sec)	Weighted arithmetic mean half-life and standard error (sec)
^{216}Po	Quartz crystal	0.143	0.003	
^{216}Po	Quartz crystal	0.146	0.004	0.145 ± 0.002
^{216}Po	60-cycle a.c.	0.147	0.005	
^{217}At-2	Quartz crystal	0.0328	0.0006	
^{217}At-1	Tuning fork	0.0320	0.0005	0.0323 ± 0.0004
^{218}Rn	Quartz crystal	0.035	0.001	—

Table 1 presents the values of the half-lives for all sets of data. Individual values of ^{216}Po and ^{217}At were weighted by the inverse square of their standard errors to calculate their respective mean half-lives. The errors quoted are statistical standard errors. They do not reflect any systematic errors that may have been made. Table 2 compares the present results with those of other investigators.

TABLE 2. COMPARISON OF HALF-LIFE MEASUREMENTS WITH EARLIER WORK

Nuclide	Half-life (sec)	Reference*
^{216}Po	0.158 ± 0.008	10
	0.145 ± 0.015	9
	0.145 ± 0.002	This work
^{217}At	0.018 ± 0.002	3,4
	0.021	15
	0.0323 ± 0.0004	This work
^{218}Rn	0.019 ± 0.002	6
	0.030 ± 0.003	8
	0.035 ± 0.001	This work

* Numbers refer to footnotes in text.

The 0.145 ± 0.002 second half-life obtained for ^{216}Po is in better agreement with the very early one measured by MOSELEY and FAJANS[9] than with the later, more commonly accepted one found by WARD[10].

The hinderance factor of ^{217}At has been calculated according to Equation (2). With values of 0.0323 ± 0.0004 sec for the half-life, 7.064 MeV[5] for the alpha-particle energy, 133.40 and −51.1913 for the astatine constants, A_z and B_z,[1,2] respectively, F was found to be 1.2.

The 0.035 ± 0.001 second half-life of ^{218}Rn agrees reasonably well with that of 0.030 ± 0.003 sec obtained by Ruiz(8). It does not agree with earlier measurements(3, 4, 15).

The method described in this paper to measure half-lives may be applied to any system where the formation and decay of the nuclide or nuclear state may be discerned in some unambiguous manner. Half-lives from 10^{-5} to 10 sec can readily be measured. Other methods become more practicable at either extreme of this range.

Acknowledgements. It is a pleasure to acknowledge the assistance of Mr. W. C. Bentley for providing the various methods of time-pulse generation. Several valuable discussions were held with Mr. B. S. Garbow on "programming" the data and with Dr. A. H. Jaffey on interpretation of the data. Mr. C. Ahlberg devoted much time in preparing the data for programming. We are also thankful to Mr. M. Oselka and other members of the Argonne Cyclotron Group for the irradiation of the thorium target.

(15) A. C. English, T. E. Cranshaw, P. Demers, J. A. Harvey, E. P. Hincks, J. V. Jelley and A. N. May, *Phys. Rev.* 72, 253 (1947).

weighed as $SrC_2O_4 \cdot H_2O$ to give the chemical yield for each separate 'milking'. In the short growth period experiments yttrium was precipitated as $Y(OH)_3$ and the strontium solution scavenged with $Fe(OH)_3$ before precipitating $SrC_2O_4 \cdot H_2O$.

The milking of yttrium daughter activities from zirconium samples was carried out using an anion exchange column [Dowex 1, 4 cm × 0.4 cm]. The carrier-free zirconium activity was back-extracted into 2 ml conc. HCl and the solution passed through the ion exchange column. KRAUS(1) has shown that from solutions 10N or higher in HCl negatively-charged chloride complexes of zirconium are adsorbed while yttrium is not. Thus by washing the column with conc. HCl after the required growth period, yttrium daughter activities were quantitatively removed, leaving zirconium on the column.

Standard end-window Geiger counters [Mullard MX 123] were used to follow the gross decay of activities. Gamma spectra were examined using a 2 in. × 1½ in. diameter NaI(Tl) crystal as detector with a single-channel analyser or a 50-channel analyser.

RESULTS AND DISCUSSION

Yttrium isotopes

The gross decay curves produced by counting yttrium samples on a Geiger counter could not be resolved satisfactorily. γ-rays from the yttrium samples were detected in the NaI(Tl) crystal and a discriminator set so that only γ-rays with energy above 1 MeV were counted. The decay curves so produced were resolved from a 14.6 hr activity into three shorter components with half-lives of about 2.6 hr, 34 min and 12 min (Fig. 2).

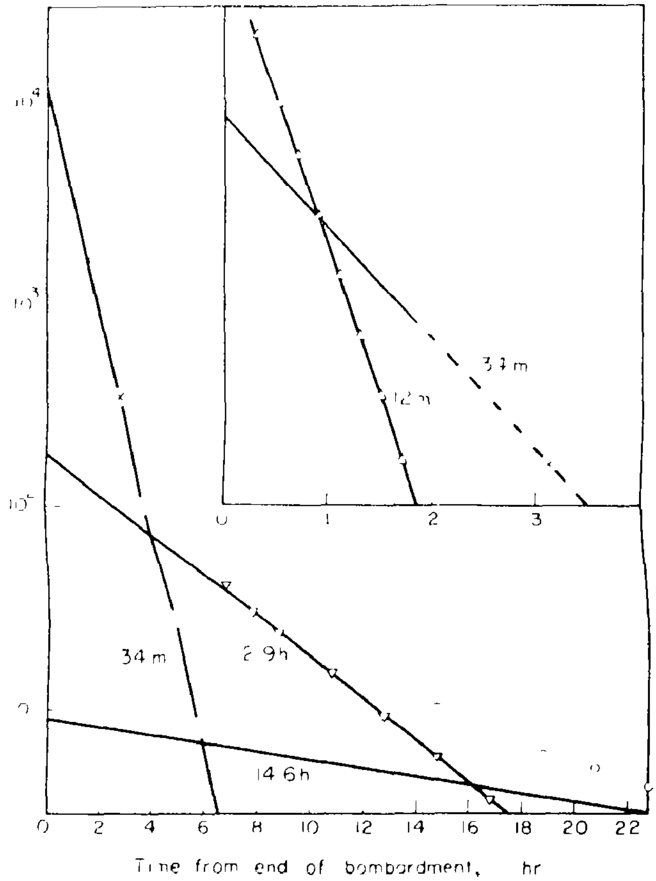


FIG. 2.—Yttrium sample, decay of gamma rays above 1.0 MeV. (The 2.9 hr half-life is an individual determination, not the mean value.)

---

(1) K. A. KRAUS and F. NELSON, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva,* 1955 Vol. 7 Paper 837. United Nations (1956).

The 14 6 hr component is assigned to ^{86}Y leaving the short half-lives unassigned and obviously disagreeing with the reported values [Fig 1 Table 1]

TABLE 1

Strontium daughter	Half-life	Yttrium parent	Half-life (CARETTO and WIIG)
^{87m}Sr	2 8 hr	^{87}Y	80 hr
^{85}Sr	65 days	^{85}Y	5 hr
^{85m}Sr	70 min		
^{83}Sr	33 hr	^{83}Y	3 5 hr
^{82}Sr	25 5 days	^{82}Y	70 min

Clearly the only way to assign a mass number to these activities was to examine the strontium decay products The chemistry used in the separations of the original yttrium activities and the subsequent strontium decay products made it impossible for any other activities, such as possible traces of radioactive rare earths derived from impurities in the yttrium, to be carried down with the strontium Thus the activities found in the strontium decay products could be used to assign a mass to, and give an indication of the half-life of, the yttrium parent activities Five activities were found to be involved [Table 1]

^{85}Y Two experiments were carried out in which the strontium daughter activity was milked from the yttrium parent, with a growth period of 1 hr between milkings In the first experiment ten milkings were made and all the samples counted for 137 days In the second, six samples were produced and counted for 70 days In both experiments all but the first two samples showed only a half-life of 65 days The resulting counting rates were corrected for decay, chemical yield, and differences in counters and the corrected yields plotted against the time of separation (Fig 3) These two experiments gave half-lives of 3 8 hr and 3 1 hr for ^{85}Y

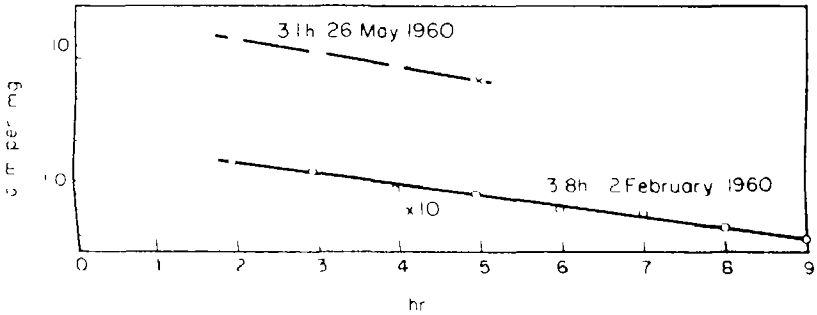


FIG 3 Yields of ^{85}Sr milked at hourly intervals from yttrium (two experiments)

In one experiment, six strontium samples were milked off at two hour intervals and the decay of the 0 225 MeV γ-ray from ^{85m}Sr, followed in each sample Plotting the corrected yields against time of separation for this activity gave a half-life of 3 08 hr for ^{85}Y (Fig 4)

In another experiment yttrium activities were produced by bombardment of a SrO target After allowing 4½ hr for decay, a pure yttrium sample was isolated and the growth and decay in it of the ^{85m}Sr 0 225 MeV γ-ray followed Fig 5 is a plot of the experimental points compared with a theoretical curve calculated from the half-lives of 70 min for ^{85m}Sr and 3 5 hr for ^{85}Y

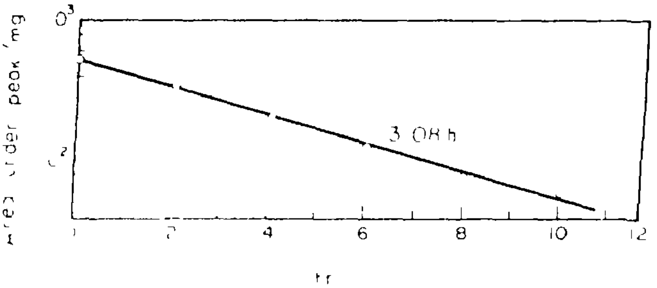


FIG. 4. Yields of ^{83m}Sr milked at 2 hr intervals from yttrium

The annihilation peak in the γ-spectra from pure yttrium samples was found to decay with a 3.5 hr half-life. Yttrium daughter activities milked from pure zirconium samples after 15 min growth also showed the annihilation radiation to decay with a 3.5 hr half-life. Our mean value from all experiments was 3.4 hr. The range of the

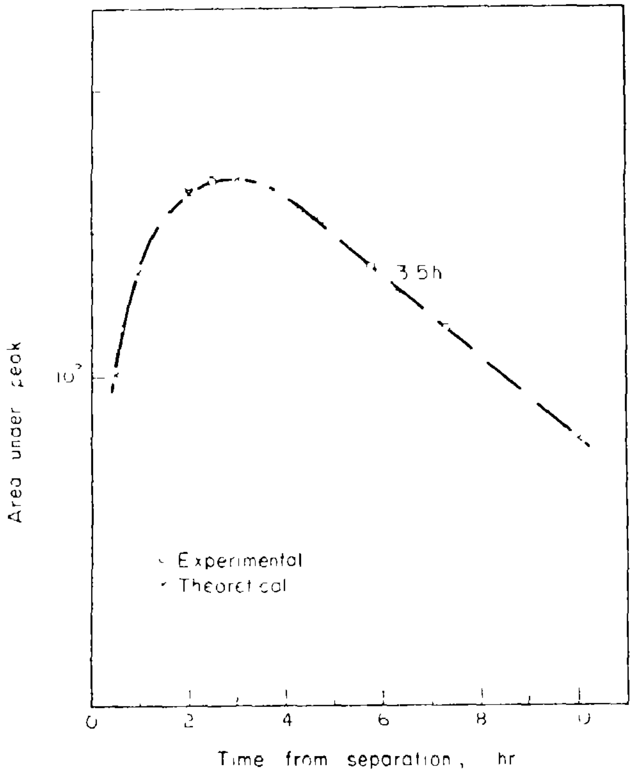


FIG. 5. Growth and decay of 0.225 MeV γ-ray from an initially pure yttrium sample

(presumed) positrons from the 3.4 hr yttrium activity, produced by milking a pure zirconium sample after 15 min growth, was found to be 1060 mg/cm^2 of aluminium, corresponding to a maximum energy of 2.4 MeV.

^{83}Y. Experiments in which strontium samples were counted on Geiger counters were difficult to perform because the samples had to be counted for a long time (five months) before the decay curves could properly be resolved. However, examination of the γ-spectra from strontium samples produced by allowing yttrium to decay for

30 min indicated a 0 76 MeV γ-ray, which decayed with a 33 hr half-life and was therefore attributed to ^{83}Sr None of the reported γ-rays from this isotope gave peaks which could be resolved In two experiments with a growth period between milkings of 20 min, six strontium samples were produced from an yttrium parent and the decay of the 0 76 MeV γ-ray followed over several days using the single-channel analyser Plots of the corrected yields against time of separation indicated half-lives of 32 9 min and 36 9 min for ^{83}Y (Fig 6)

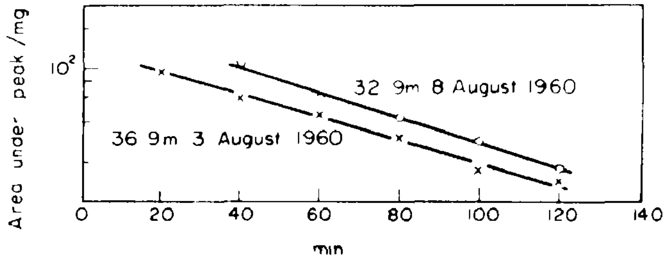


Fig 6 Yields of ^{83}Sr milked at 20 min intervals from yttrium (two experiments)

A γ-ray of energy 0 98 MeV was found in an yttrium sample to decay with a half-life of 39 min, and is therefore assumed to be associated with the decay of ^{83}Y

Thus the 34 7 ± 1 6 min [standard deviation] activity found in the decay of high-energy γ-rays from an yttrium sample is assigned to ^{83}Y The half-life is the mean of six experiments No evidence of annihilation radiation decaying with this half-life could be found so presumably ^{83}Y decays mainly by electron capture

^{82}Y In the experiment in which strontium daughter activity was milked from the yttrium parent at one hour intervals, only the first two samples indicated a 25-day component From these experiments it was estimated that the half-life of ^{82}Y must be less than 14 min To measure the half-life more accurately, an experiment was carried out in which six strontium milkings were made at 20-min intervals, and the strontium samples were counted for six months After this time correction was made for the amount of 65-day activity present, and the corrected yields of the 25 day ^{82}Sr activity indicated a half-life of 12 3 min for ^{82}Y (Fig 7)

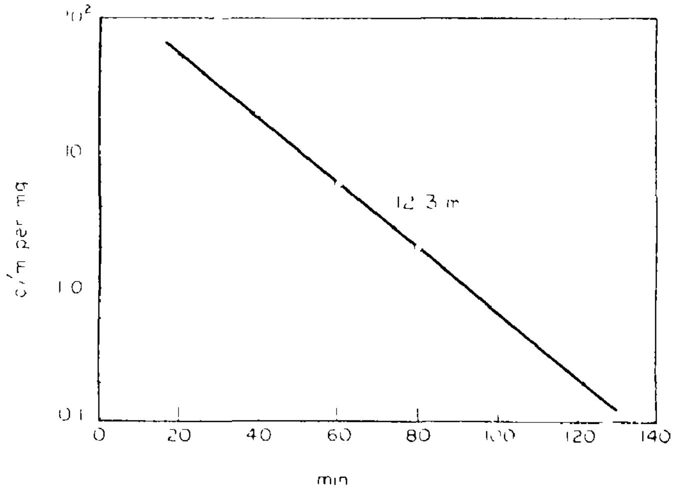


Fig 7 —Yields of ^{82}Sr milked at 20 min intervals from yttrium

Thus the 12.3 ± 0.2 min activity (mean of five experiments) found in the decay of γ-rays above 1.0 MeV from yttrium samples is assigned to ^{82}Y.

^{84}Y. *The milking experiments described above gave no indication of an yttrium parent with a half-life of 2.6 hr. An experiment was therefore carried out to try and confirm the assignment of a 3.7 hr positron activity to ^{84}Y by* ROBERTSON *et al.*(6) *The Birmingham 60-in. cyclotron was used to bombard a target of 0.9 mg ^{84}Sr oxalate* [containing 0.441 mg ^{84}Sr] with 5 MeV protons, the yttrium fraction was separated and counted for 42 days. The decay curve was resolved into three components of half-lives 80 hr (assigned to ^{87}Y), 14.6 hr (^{86}Y) and an activity which was consistent with a mixture of 2.6 hr and 3.4 hr activities. The latter would be ^{85}Y from a ^{84}Sr(p, γ) reaction and the former would be due to ^{84}Y produced by the reaction ^{84}Sr*

TABLE 2

Nuclide	Half-life CARETTO and WIIG	This work
^{86}Y		14.6 hr
^{85}Y	5 hr	3.4 hr
^{84}Y	–	2.6 hr
^{83}Y	3.5 hr	34.7 min
^{82}Y	70 min	12.3 min

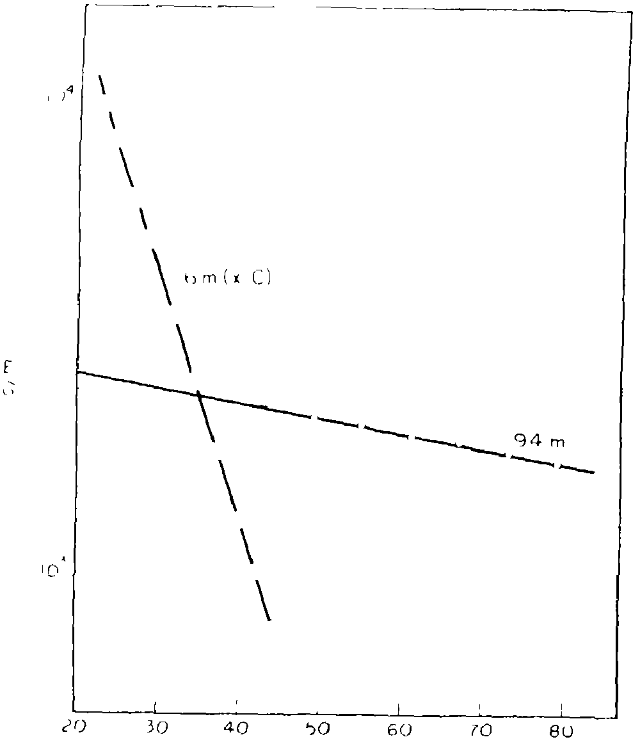


FIG. 8 - Zirconium sample, decay of γ-rays above 0.6 MeV

---

* Supplied by A.E.R.E. Harwell

(6) B. E. ROBERTSON, W. E. SCOTT and M. L. POOL, *Phys. Rev.* 76, 1649 (1949)

(*p*, *n*), and the same as the 2.6 ± 0.5 hr activity (mean of six experiments) found in the decay of high-energy γ-rays from a pure yttrium sample. Table 2 summarizes our results for comparison with those of CARETTO and WIIG.

Zirconium isotopes

By counting all γ-rays above 0.6 MeV (to exclude the 0.59 MeV γ-ray from ^{89m}Zr) from a pure zirconium fraction, two experiments gave evidence for a short-lived *activity with a 6 min half-life (Fig. 8). The 94 min component in Fig. 8 is attributed to* ^{87}Zr.

Milking of yttrium from zirconium was difficult to perform, as it was found to be impossible to get a pure zirconium fraction on to the anion exchange column in under 42 min from the end of bombardment. As only the first two milkings of yttrium taken at 20-min intervals showed any 3.4 hr component in the gross decay, only an estimate could be made of the parent half-life. The first milking was made after 20 min, i.e. 62 min from the end of bombardment. The second milking made 82 min from the end of bombardment has very little 3.4 hr activity associated with its decay, thus the short-lived component must probably have had a half-life between 6 and 8 min.

To assign a mass to this short-lived activity, a pure zirconium fraction produced 41 min after the end of bombardment was milked of its yttrium decay products 30 min later, i.e. at $t = 71$ min. At $t = 101$ min a second yttrium milking was carried out. At $t = 131$ and 161 min the first and second yttrium fractions respectively were milked of their strontium decay products, i.e. the original zirconium granddaughter decay products. The gamma spectra from the first, but not the second, strontium sample clearly indicated the 0.225 MeV γ-ray from ^{85m}Sr, thus a short lived activity with a half-life of about 6 min is assigned to ^{85}Zr.

A careful examination of the γ-spectra from Zr samples failed to indicate the existence of the 0.35 and 0.65 MeV γ-rays from ^{87}Zr, reported by ROBERTSON *et al.*(5) However a 1.2 MeV γ-ray was found to decay with a 90 min half-life and is therefore assigned to ^{87}Zr.

[illegible] Nucl Chem , 1963, Vol 25, pp 159 to 163 Pergamon Press Ltd Printed in Northern Ireland

ELECTRONIC STRUCTURE AND SPECTRA OF TETRAHALOGENOFERRATES (II)

C Furlani, E Cervone and V Valenti
Institute of General Chemistry, University of Rome

(*Received* 13 *June* 1962)

Abstract—The spectrum of the tetrahedral complex $[FeCl_4]^{=}$ consists of only one, rather intensive d-d band in the near infrared region which is assigned to the transition $^5E \rightarrow {}^5T_2$ (T_d), and has $\lambda_{max} \sim$ 2.47 μ with log E_{mol} = 1,9 Suitable solvents for spectroscopic absorption measurements in this region are CD_3NO_2 or $ClCH_2CN$

TETRAHALOGENOFERRATES (II), a member of the recently discovered family of tetrahedral halogenocomplexes of transition metal ions, have been prepared for the first time by NYHOLM, GILL and coworkers$^{(1\ 2\ 3)}$ who demonstrated their tetrahedral structure and described also several physico-chemical properties of these compounds, but did not report their complete spectra, nor their interpretation Continuing our previous researches on the absorption spectra of tetrahedral halogenocomplexes of transition metals, we independently prepared some new tetrachloroferrates (II) and measured their absorption spectra in the visible and near infra-red region We found that all salts containing the anion $[FeCl_4]^{2-}$ do not absorb in the visible region (they appear almost perfectly white in the solid state) but have one ligand field band with a maximum in the region around 4000 cm^{-1} (Fig 1) Such a band is undoubtedly due to a transition between the two sublevels ^5E (ground state) and $^5T_2$, originated from the splitting of the ground term ^5D of Fe^{2+} under a ligand field of symmetry T_d The best Δ value to fit the experimentally observed frequency in the scheme of intermediate coupling appears to be 4000 cm^{-1}, and it corresponds perfectly to the theoretical expectation for a tetrahedral complex of magnetically normal Fe^{2+} and Cl^- as the ligand ($\Delta_{octahedral}$ in $[Fe(H_2O)_6]^{2+}$ is about 10400 $cm^{-1(4\ 5)}$, so $|\Delta_{tetrahedral}|$ is expected to be a little less than $\frac{4}{9}$ of this value, owing to the position of Cl^- after H_2O in spectrochemical series) The ratio $\Delta(MeCl_4{}^{2-})/\Delta(Me\,aq_6{}^{2+})$ is 0.385, in perfect agreement with values quoted by COTTON *et al* $^{(6)}$ for other transition metals

It has to be remarked that such a Δ value for Fe^{2+} is among the highest values observed for similar tetrahedral complexes of the first row of transition metals* but nevertheless the only absorption band of $[FeCl_4]^{2-}$ lies relatively far in the infrared

The intensity of the observed band is rather high (E_{mole} = 80 ∓ 3 in chloroacetonitrile solutions), as in other tetrahedral halogenocomplexes, thus confirming the tetrahedral structure of $[FeCl_4]^{2-}$ The band is a single one, and appears to be symmetrical although we cannot exclude the possible presence of satellites on its low-frequency side we take this fact as an indication that Jahn-Teller distorsions of the $[FeCl_4]^{2-}$ tetrahedron, although theoretically expected, are probably not very conspicuous (see also Reference 3) Actually, the calculated scheme of energy levels according to the theory of intermediate coupling predicts a splitting of the upper level

---

* Typical values are $[CoCl_4]^{2-}$ Δ ~ 3200 cm^{-1} (8), $[NiCl_4]^{2-}$, Δ ~ 3700 cm^{-1} (9), $[MnCl_4]^{2-}$, Δ ~ 3300 cm^{-1} (10)

(1) N S GILL, R S NYHOLM and P PAULING *Nature, Lond* **182,** 168 (1958)
(2) N S GILL and R S NYHOLM, *J Chem Soc* 3997 (1959)
(3) N S GILL, *J Chem Soc* 3512 (1961)
(4) C FURLANI, *Gazz Chim Ital* **87,** 371 (1957)
(5) C K JORGENSEN, *Acta Chem Scand* **8,** 1502 (1954)
(6) F A COTTON, D M L GOODGAME and M GOODGAME *J Amer Chem Soc* **84,** 167 (1962)

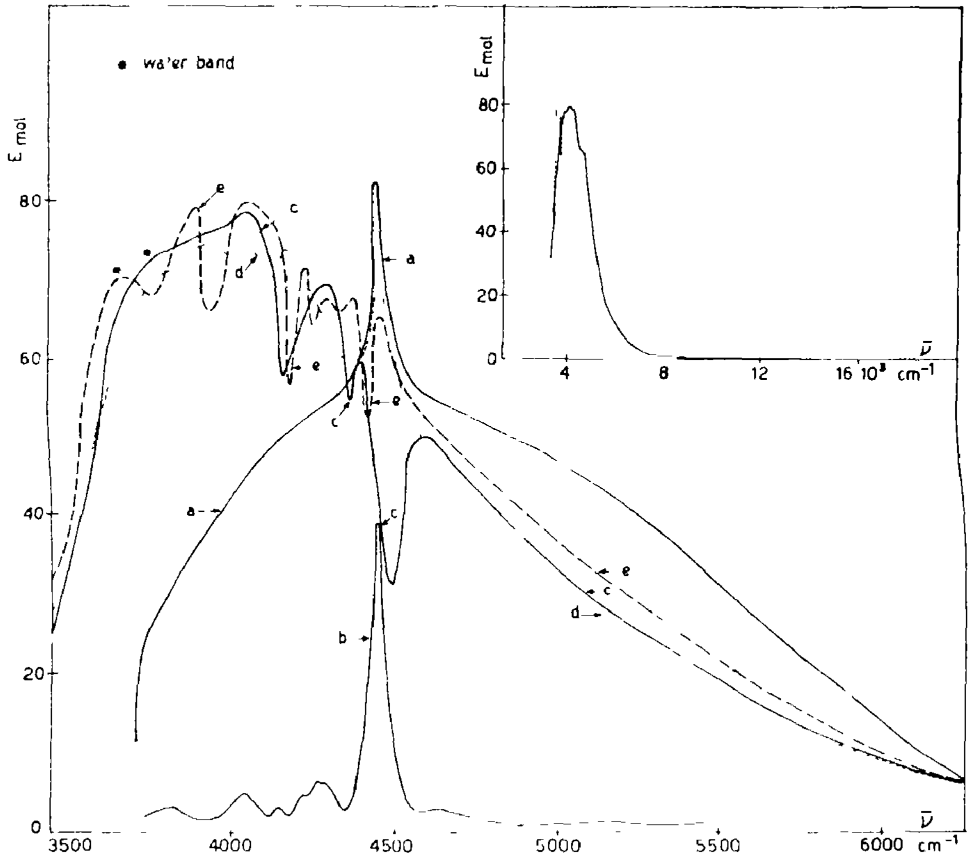


Fig 1 —Absorption spectra of (a) $[C_6H_5CH_2N(CH_3)_3]_2[FeCl_4]$ solid in C_4Cl_6 mull, (b) $[(C_6H_5CH_2N(CH_3)_3]Cl$ solid in C_4Cl_6 mull, (c) $[C_6H_5CH_2N(CH_3)_3]_2[FeCl_4]$ in CH_3NO_2, (*d*) $[C_6H_5CH_2N(CH_3)_3]_2[FeCl_4]$ in CD_3NO_2, (e) $[C_6H_5CH_2N(CH_3)_3]_2$-$[FeCl_4]$ in $ClCH_2CN$, (a), (b) arbitrary ordinate scale, (b), (d), (e) in presence of excess $[C_6H_5CH_2N(CH_3)_3]Cl$

(${}^5\Gamma_2$ under T_d), owing to spin orbit coupling effects, into several sublevels grouped into three multiplets, over a range of approximately 500 cm^{-1} (see Fig 2), but we think that all these sublevels are contained under the observed single band envelope Minor variations in the position of the maximum according to the solvent used, to the nature of the cation bound to the $[FeCl_4]^{2-}$ anion or to the aggregation state of the complex (see Table), have been observed, but they are probably due to second-sphere environmental effects, they are in our opinion perfectly compatible with the scheme of interpretation discussed above

The absorption intensity follows satisfactorily the Lambert-Beer law only in the presence of an excess of free Cl^- ions, otherwise dilute solutions of $[FeCl_4]^{2-}$ salts exhibit decomposition, as is evident from the lowering of the apparent E_{molar} value at

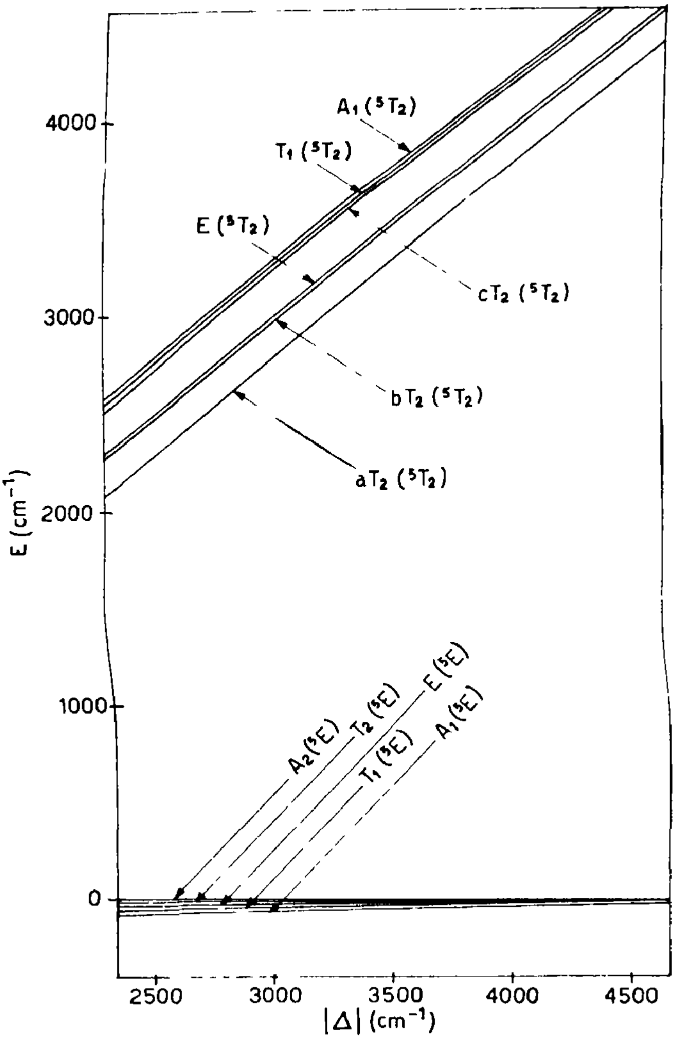


FIG. 2 Term system of the lowest energy levels (sublevels of ^5D) of Fe^{2+} in tetrahedral complexes with spin orbit coupling (λ 90 cm^{-1}), zero of the ordinate scale corresponds to $E(^5E)$ under T_d without spin orbit coupling

ABSORPTION SPECTRA OF TETRACHLOROFERRATES

Compound	Solvent	$\bar{\nu}_{\max}$ (cm^{-1})	$\varepsilon_{\max}$ (mole)
$[C_6H_5CH_2N(CH_3)_3]_2FeCl_4$	Reflexion spectrum	4490	
$[C_6H_5CH_2N(CH_3)_3]_2FeCl_4$	C_4Cl_6 mull	4440	-
$[C_6H_5CH_2N(CH_3)_3]_2FeCl_4$	CH_3NO_2*	4050	78 ± 5
$[C_6H_5CH_2N(CH_3)_3]_2FeCl_4$	CD_3NO_2*	4050	75 ± 5
$[C_6H_5CH_2N(CH_3)_3]_2FeCl_4$	$ClCH_2CN$*	4050	80 ± 3
$[(CH_3)_4N]_2FeCl_4$	Reflexion spectrum	4480	
$[(CH_3)_4N]_2FeCl_4$	C_4Cl_6, mull	3880	
$[(CH_3)_4N]_2FeCl_4$	$ClCH_2CN$	4060	61 ± 10
$[(C_6H_5)_4As]_2FeCl_4$	Reflexion spectrum	4550	
$[(C_6H_5)_4As]_2FeCl_4$	$ClCH_2CN$	4060	77 ± 3

* In presence of excess $[C_6H_5CH_2N(CH_3)_3]Cl$

the maximum. Therefore, addition of halide ions in excess appears to have a beneficial effect on the stability of the tetrahedral structure in solution, as has been observed also with other tetrahalogenocomplexes[(6,7,8,9)], and prevents also other possible ways of decomposition. In this respect, while solid salts containing the $[FeCl_4]^{2-}$ anion are remarkably stable in dry air, their solutions in polar organic solvents, which are colourless or only slightly yellowish when freshly prepared, become sometimes brown and undergo evident although not immediate decomposition, especially in contact with air. Among the decomposition products are $[FeCl_4]^-$ salts, which can be detected by the presence of their characteristic absorption pattern in the 500–800 mμ region, but the decomposed solutions of $[FeCl_4]^{2-}$ are a brown colour which is quite different from the greenish-yellow colour of $[FeCl_4]^-$, and therefore must contain also other decomposition products, e.g. pseudo-octahedral solution products. However, this type of decomposition occurs much less seriously and much more slowly, or can even be completely prevented, in the presence of an excess of free chloride ions.

EXPERIMENTAL

Preparation of tetrachloroferrate (II) salts. On mixing stoicheiometric amounts of anhydrous $FeCl_2$ and of an onium chloride in absolute ethanol, usually the chloroferrate(II) precipitates spontaneously. Since the compounds are not extremely sensitive to oxidation, exclusion of air is not strictly necessary, but it helps in obtaining purer and white products; this is important, since it is often difficult if not impossible to recrystallize tetrachloroferrates (II). Following this procedure we prepared bis-trimethylbenzylammonium tetrachloroferrate (II) $[C_6H_5CH_2N(CH_3)_3]_2[FeCl_4]$, a cream white solid (Found: C, 48.06; H, 6.55; N, 5.13; Fe, 11.14; Cl, 28.70. Calc. for $C_{20}H_{32}N_2FeCl_4$: C, 48.21; H, 6.43; N, 5.62; Fe, 11.21; Cl, 28.53%), bis-tetramethylammonium tetrachloroferrate (II) $[(CH_3)_4N]_2[FeCl_4]$, which is perfectly white (Found: C, 27.86; H, 6.74; N, 7.92; Fe, 16.05; Cl, 40.70. Calc. for $C_8H_{24}N_2FeCl_4$: C, 27.76; H, 6.94; N, 8.10; Fe, 16.14; Cl, 41.06%) and bis-tetraphenylarsonium tetrachloroferrate (II) $[(C_6H_5)_4As]_2[FeCl_4]$, pale yellow (Found: C, 60.30; H, 4.01; Fe, 5.46; Cl, 14.33. Calc. for $C_{48}H_{40}As_2FeCl_4$: C, 59.76; H, 4.15; Fe, 5.79; Cl, 14.73%). For the sake of comparison with the spectra of decomposed solutions, we prepared also a complex of Fe(III), namely trimethylbenzylammonium tetrachloroferrate (III) $[C_6H_5CH_2N(CH_3)_3][FeCl_4]$, pale green needles crystallizable from alcohol (Found: C, 33.86; H, 4.81; N, 4.20; Fe, 16.26; Cl, 40.40. Calc. for $C_{10}H_{16}NFeCl_4$: C, 34.50; H, 4.60; N, 4.02; Fe, 16.04; Cl, 40.83%). All tetrachloroferrates (II) are readily and completely decomposed by water, and to a smaller extent also by alcohols, but are soluble in polar organic solvents, including CH_3NO_2, CH_3CN, dimethylformamide, dimethylsulphoxide and chloroacetonitrile. As in other series of tetrahalogenometallates (II) of transition metals[(8,9)] the tetramethylammonium salt is by far the least soluble of all. All tetrachloroferrates (II) we prepared behave as 1:2 electrolytes in nitromethane and have a magnetic moment which is a little higher than the spin-only value for four unpaired electrons, as reported by Gill[(3)].

Spectroscopic measurements. Preliminary confirmation of the existence and position of an absorption band in the near infra-red region (4000–5000 cm^{-1}) was obtained by the spectra of solid tetrachloroferrate (II) salts, either reflection spectra of the powdered substances, or spectra in hexachlorobutadiene mulls. More exact and quantitative observation of the absorption spectra in solution was difficult because of two factors which are always a serious obstacle to spectrophotometric measurements in the region below 5000 cm^{-1}: (a) a strong disturbance caused by water absorption at 2.7–2.8 μ, which can be removed only by extreme care in purging both the apparatus and the solution from traces of water; (b) opacity of the solvents. Most common solvents contain hydrogen, and their stretching modes correspond to more or less intense absorptions below 4 5000 cm^{-1}; for this reason the use of solvents like dimethylsulphoxide, acetonitrile and dimethylformamide had to be discarded. Nitromethane absorbs less strongly than the previous solvents and can be used within certain limitations as a solvent, especially in thin layers (absorption cells of 1 mm or less). An improvement can be made by the use of deuterated nitromethane CD_3NO_2, which we prepared from CH_3NO_2 and D_2O by Wilson's[(10)] method; it still absorbs in the region 2.7–2.8 μ, as does nitromethane, but the

---

[(7)] F. A. Cotton, D. M. L. Goodgame and M. Goodgame *J. Amer. Chem. Soc.* **83**, 4690 (1961).

[(8)] C. Furlani and G. Morpurgo, *Z. Phys. Chem. N.F.* **28**, 93 (1961).

[(9)] C. Furlani and A. Furlani, *J. Inorg. Nucl. Chem.* **19**, 51 (1961).

[(10)] T. P. Wilson, *J. Chem. Phys.* **11**, 361 (1943).

absorption bands of CH_3NO_2 at 2 2-2 3 μ and at 2 4 μ are greatly reduced in intensity, so the opacity of the solvent is also greatly reduced Good results are obtained also by the use of chloroacetonitrile as a solvent, although $ClCH_2CN$ has several intense absorption bands between 2 and 3 μ (at 2 20, 2 35 2 54, 2 67 μ), they are very narrow, and obscure only a few narrow frequency intervals in that region, so that the contour of a rather broad absorption band, as is that of $[FeCl_4]^{2-}$, can be completely identified, chloroacetonitrile has the additional advantage of being a very good solvent, where fairly concentrated solutions of halogenocomplexes can be prepared, thus allowing use of very thin absorption cells and further improving the total transparency of the solvent The vibrational spectrum of the onium cations can be sometimes observed as a system of narrow bands superimposed to the envelope of the much broader *d-d* band of the anion

Most measured spectra were of the trimethylbenzylammonium salt in the presence of the corresponding chloride, which are both easily soluble in the solvents mentioned above, the tetramethylammonium salt is much less soluble, and the tetraphenylarsonium tetrachloroferrate is itself well soluble, but tetraphenylarsonium chloride is not, and the complex could be measured only in presence of a very small excess of free Cl^- ions Spectroscopic results could be obtained for all three mentioned tetrachloroferrates (II), and no significant difference between them was detected (see Table) except a shift of ~400 cm^{-1} in passing from solutions to the solid state and a somewhat lower extinction coefficient for the tetramethylammonium salt

Ligand-field calculations The term system of Fe^{2+} was calculated only for the split terms of ^5D under a field of tetrahedral symmetry with spin-orbit coupling, in two weak-field approximations, i e $(SLM_SM_L) \rightarrow (SLJM_J) \rightarrow (\Gamma M_\Gamma M_J)$ and $(SLM_SM_L) \rightarrow (S\Gamma M_SM_\Gamma) \rightarrow (\Gamma M_\Gamma M_J)$, which gave exactly coincident results, matrix elements for the first reckoning scheme can be found in Griffith⁽¹¹⁾ and for the second one in CONDON and SHORTLEY⁽¹²⁾ Theory of the atomic spectra", Cambridge Univ Press 1953 Since the ligand field interactions due to tetrahedral environment represent a very weak perturbation we are confident that the adoption of a weak-field scheme and our neglecting the higher levels of lower spin multiplicity are fully justified We assumed $\zeta = 360$ cm^{-1} or $\lambda = 90$ cm^{-1} (a slightly smaller value than in free Fe^{2+}), and varied Δ_{tetr} between 2500 and 4500 cm^{-1} As is evident from Fig 2 the tetrahedral ground state $^5E(\Gamma_3)$ is left still practically degenerate by the spin-orbit perturbation, whereas the upper state $(^5T_2, \Gamma_5)$ is split to a much larger extent, the best Δ value which can fit the average experimental frequency is 4000 cm^{-1}

Acknowledgement—The present work has been carried out under financial support by NATO through a NATO Research grant

⁽¹¹⁾ J S GRIFFITH, *Theory of Transition Metal Ions* Camb Univ Press (1961)

⁽¹²⁾ CONDON and SHORTLEY, *Theory of Atomic Spectra* Camb Univ Press (1953)

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 165 to 170. Pergamon Press Ltd. Printed in Northern Ireland

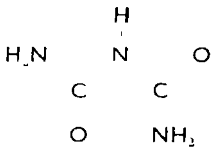
INFRA-RED ABSORPTION SPECTRA AND STRUCTURE OF BIURET–HYDROGEN PEROXIDE COMPLEXES

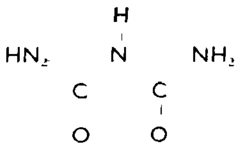
K. AIDA
The Chemical Research Institute of Non-Aqueous Solutions, Tohoku University,
Sendai, Japan

(Received 4 May 1962; in revised form 16 July 1962)

Abstract—Two complexes of biuret and hydrogen peroxide, $(C_2H_5N_3O_2)_5H_2O_2$ and $(C_2H_5N_3O_2)_5(H_2O_2)_2$, have been prepared. The infrared absorption spectra and the X-ray diffraction patterns of these complexes are quite similar to those of biuret hydrate. Consequently, it has been concluded that the biuret molecules in these complexes have the trans configuration and make up inclusion compounds as is the case in biuret hydrate. The differences between complexes of urea hydrogen peroxide and biuret-hydrogen peroxide are discussed.

IN a previous report,[1] the author has shown that the biuret molecule can exist in at least two forms. One is found in biuret hydrate (α-form) and the other in anhydrous biuret (β-from). In the former case, an X-ray analysis has been carried out by HUGHES *et al.*[2] and it was found that α-biuret has the trans configuration with the amide groups inclined slightly to each other. In the case of β-form, no structural study has yet been reported, but the following cis configuration was proposed[1] from the analogy to diacetamide[3] and from the infra-red absorption spectra of its metal complexes.[1]


α-form


β-form

Biuret forms complexes with hydrogen peroxide as its mother compound, urea, does. The purpose of this study is to obtain evidence relating to the configuration of the biuret molecules in these complexes. Also, it appears worthwhile to compare the structure of biuret-hydrogen peroxide with that of urea-hydrogen peroxide.

EXPERIMENTAL

A biuret-hydrogen peroxide complex was first prepared by STOLTZENBERG[4] in 1916 and had the composition of (5 to 1). Besides this, a (5 to 2) complex is known to be formed by changing slightly the crystallizing conditions. Crystals crystallized slowly under the conditions of STOLTZENBERG are transparent needles and have the composition of (5 to 1). However, those crystallized rapidly from more concentrated hydrogen peroxide solutions are white opaque needles and have the composition of (5 to 2). The analyses of the compounds used in the present work are as follows.

Transparent crystals. Calcd. for $(C_2H_5N_3O_2)_5H_2O_2$: C, 21.9; H, 5.0; H_2O_2, 6.2%. Found: C, 21.0, 21.5; H, 5.1, 5.0; H_2O_2 (iodometry), 6.4, 6.5%.

Opaque crystals. Calcd. for $(C_2H_5N_3O_2)_5(H_2O_2)_2$: C, 20.6; H, 5.0; H_2O_2, 11.7%. Found: C, 20.8, 20.8; H, 5.0, 5.2; H_2O_2 (iodometry), 11.8, 12.5%.

---

[1] K. AIDA, *J. Inorg. Nucl. Chem.* **23**, 155 (1961).
[2] E. W. HUGHES, H. L. YAKEL and H. C. FREEMAN, *Acta Cryst.* **14**, 345 (1961).
[3] T. UNO and K. MACHIDA, *Bull. Chem. Soc. Japan* **34**, 545 (1961).
[4] H. STOLTZENBERG, *Ber. Dtsch. Chem. Ges.* **49**, 1545 (1916).

[illegible] used was prepared according to the procedure [illegible] H_2O_2 [illegible] for $CO(NH_2)_2$ [illegible]

Infra-red absorption spectra were measured in Nujol and in hexachlorobutadiene mulls (in their proper regions (except urea for which KBr pellet technique was used) by means of a Perkin-Elmer Model 21 Spectrophotometer with a sodium chloride prism.

X-ray diffraction patterns were obtained on powdered samples by means of a Shimadzu Geigerflex X-ray Diffractometer with nickel-filtered Cu K_α radiation.

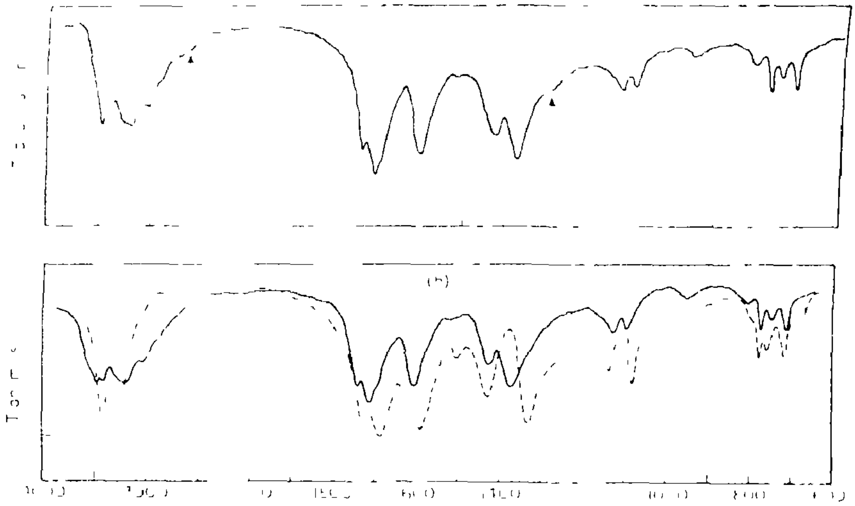


Fig. 1 Infra-red absorption spectra of (a), biuret-hydrogen peroxide, (b), biuret hydrate (solid line) and anhydrous biuret (broken line)

RESULTS AND DISCUSSION

The infra-red absorption spectrum of $(C_2H_5N_3O_2)_5 H_2O_2$ is shown in Fig. 1a. $(C_2H_5N_3O_2)_3 (H_2O_2)_2$ gives an almost identical curve which is not shown. Observed frequencies are listed in Table 1 together with those of biuret hydrate and anhydrous biuret.(1) On comparing the spectrum with those of biuret hydrate (Fig. 1b, solid line) and anhydrous biuret (Fig. 1b, broken line), it is easily seen that it is quite similar to that of the biuret hydrate. As stated above, the biuret molecules in biuret hydrate exist in α-form. Consequently, it can be said that the biuret molecules in $(C_2H_5N_3O_2)_5 H_2O_2$ and $(C_2H_5N_3O_2)_3 (H_2O_2)_2$ also exist in α-form.

By close examination of the curve in Fig. 1a, it is seen that there are weak absorptions around the places indicated by arrows which are not found in Fig. 1b. These absorptions become slightly stronger in the case of $(C_2H_5N_3O_2)_3 (H_2O_2)_2$ and therefore these must be due to H_2O_2. This point will be discussed in connection with the urea hydrogen peroxide complex. Assignments of the frequencies of the biuret itself will be reported later together with the results of the deuterated biuret.

In Fig. 2, infra-red absorption spectra of urea (broken line) and its hydrogen peroxide complex (solid line) are shown. As is seen from this figure, the situation is quite different from the case of the biuret, that is, marked differences are observed between curves of urea and its complex. Observed frequencies and their assignments are given

---

(6) C. Lu, E. W. Hughes and P. A. Giguère, *J. Amer. Chem. Soc.* **63**, 1507 (1941)

TABLE 1.—OBSERVED FREQUENCIES (CM^{-1}) OF BIURET-HYDROGEN PEROXIDE AND BIURET

Biuret-hydrogen peroxide	Biuret hydrate[1]	Anhydrous biuret[1]
	3500 *sh*, *br*	
3468 *s*	3465 *s*	
3402 *s*	3400 *s*	3402 *vs*
3220 *s*, *br*	3220 *s*, *br*	3250 *s*, *br*
3010 *w*, *sh*	3020 *w*, *sh*	
		2820 *vw*
2630 *vw*		
		2020 *vw*
1740 *s*	1740 *s*	
1710 *vs*	1710 *vs*	1725 *vs*
		1683 *vs*
		1622 *s*
1600 *s*	1600 *s*	1585 *s*
		1495 *m*
1415 *m*	1411 *m*	1422 *s*
1360 *s*	1356 *s*	
		1326 *vs*
1290 *w*, *br*		
1118 *w*	1124 *w*	1132 *w*
1088 *w*	1090 *w*	1077 *m*
955 *vw*	952 *w*	945 *w*
880 *vw*		
804 *w*	800 *w*	795 *w*
		775 *m*
767 *m*	765 *m*	764 *m*
740 *w*	738 *w*	
708 *m*	706 *m*	714 *m*
		675 *w*

vs, very strong, *s* strong, *m*, medium, *w* weak, *vw* very weak, *sh* shoulder, *br*, broad

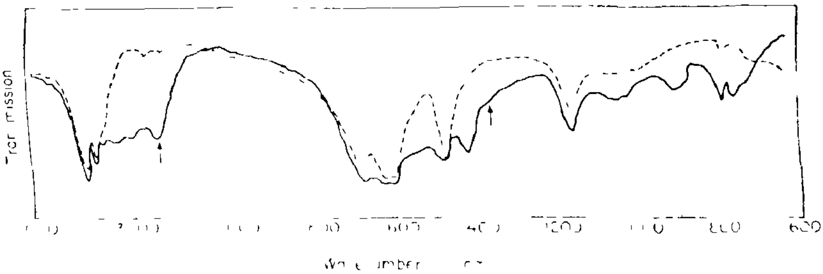


FIG. 2.—Infra-red absorption spectra of urea (broken line) and urea-hydrogen peroxide (solid line)

in Table 2. Assignments of the frequencies of urea are taken from the paper of YAMAGUCHI(6). Those bands designated by * are not discussed by her and their assignments are, therefore, taken from the paper of STEWART(7).

There is a resemblance between the spectrum of the urea-hydrogen peroxide complex and those of metal complexes in which the coordination has occurred through the nitrogen atom of the urea molecule[(8,9)] For instance in dichloro-bis-(urea)-platinum (II) and dichloro-bis-(urea)-palladium (II), the bonded NH stretching vibrations are observed at 3130, 3030 cm^{-1} and 3140, 3030 cm^{-1}, respectively[(8)] In the case of the urea hydrogen peroxide complex, these appear at 3100 and 2960 cm^{-1} In the same way, those bands at 1410 and 900 cm^{-1} in the hydrogen peroxide complex correspond to the bonded CN stretching vibrations which are observed at 1395 and 896 cm^{-1} in the platinum complex and at 1400 and 910 cm^{-1} in the palladium complex, respectively[(8)] In other words, there appear to be fairly strong hydrogen bonds of the $N{-}H \cdots O$ type in the urea hydrogen peroxide complex According to the result of the X-ray study,[(5)] there are at least two types of hydrogen bonds, the CO group in urea also forming a hydrogen bond to hydrogen peroxide molecule However, as far as the infra-red spectrum is concerned, the strength of this bond seems to be of the same magnitude as that of the bond formed between urea molecules, because no distinguishable change is observed in the carbonyl stretching region between urea and its hydrogen peroxide complex

---

(6) A. YAMAGUCHI, *J. Chem. Soc. Japan Pure Chem. Section*, **78**, 1319, 1467 (1957); A. YAMAGUCHI, T. MIYAZAWA, T. SHIMANOUCHI and S. MIZUSHIMA, *Spectrochim. Acta*, **10**, 170 (1957).

(7) J. E. STEWART, *J. Chem. Phys.* **26**, 248 (1957).

Table 2 Observed frequencies (cm^{-1}) of $CO(NH_2)_2$ and $CO(NH_2)_2 \cdot H_2O_2$

$CO(NH_2)_2$		$CO(NH_2)_2 \cdot H_2O_2$	
ν	assignments[(6,7)]	ν	assignments
3445		3442	
3342	NH_2 st	3343	NH_2 st
3240		3260	
		3100	NH_2 (bonded) st
		2960	
		2740	due to H_2O_2
1677	CO st NH_2 def	1675	CO st NH_2 def
1625	NH_2 def	1630	NH_2 def
1600	NH_2 def CO st	1605	NH_2 def CO st
1467	CN st	1480	CN st
		1410	CN (bonded) st
		1365	due to H_2O_2
1152	NH_2 rock	1156	NH_2 rock
*1050	NH_2 rock	1045	NH_2 rock
1000	CN st	1015	CN st
		900	CN (bonded) st
		880	due to H_2O_2
*785	skeletal	785	skeletal
		757	NH_2 wag
*700	NH_2 wag		

The fact that fairly strong hydrogen bonds exist in the urea hydrogen peroxide complex and no such bonds in the biuret hydrogen peroxide complexes should be reflected in the vibrations of hydrogen peroxide Unfortunately, some of the absorptions of hydrogen peroxide are overlapped with those of urea or biuret The observed frequencies are listed in Table 3

In the case of the urea complex, there appears a strong and broad absorption at about 2750 cm^{-1} which very likely is due to the hydrogen bonded OH stretching

---

[(8)] R B Penland, S Mizushima, C Curran and J V Quagliano, *J Amer Chem Soc* **79**, 1575 (1957)

[(9)] D Buismrov, T Sumarokova and V Filimokov, *Opt Spektrosk* **9**, 460 (1960) vibration This vibration occurs at about 3400 cm^{-1} in pure liquid hydrogen peroxide, but strong hydrogen bonding of —O—H N type in the urea complex probably has resulted in the shift of this vibration and has broadened it There is a weak band at 2780 cm^{-1} in pure liquid hydrogen peroxide which is assigned as a combination tone The corresponding band in the urea complex may be covered by the above mentioned bonded OH stretching absorption In the table, the frequencies of the hydrogen peroxide itself are also included which are taken from the study of GIGUERE[(10)] As is seen from the table, the observed frequencies of the hydrogen peroxide in the urea complex are somehow closer to those of the liquid hydrogen peroxide, while in the case of the biuret complexes, they are closer to the hydrogen peroxide vapour This is exactly what is anticipated, for the strong hydrogen bonds between urea and hydrogen peroxide would tend to shift the frequences of the latter closer to those of the liquid while the weaker interaction in the case of biuret and hydrogen peroxide would result in the frequencies being closer to those of the vapour

TABLE 3 —ABSORPTION OF HYDROGEN PEROXIDE (CM^{-1})

Free[(10)]		In	In
Vapour	Liquid	$CO(NH_2)_2\,H_2O_2$	$(C_2H_5N_3O_2)_5\,H_2O_2$
3590	3400	2740	overlapped
2630	2780	(2740)	2630
1255	1350	1365	1290
877	880	880	880

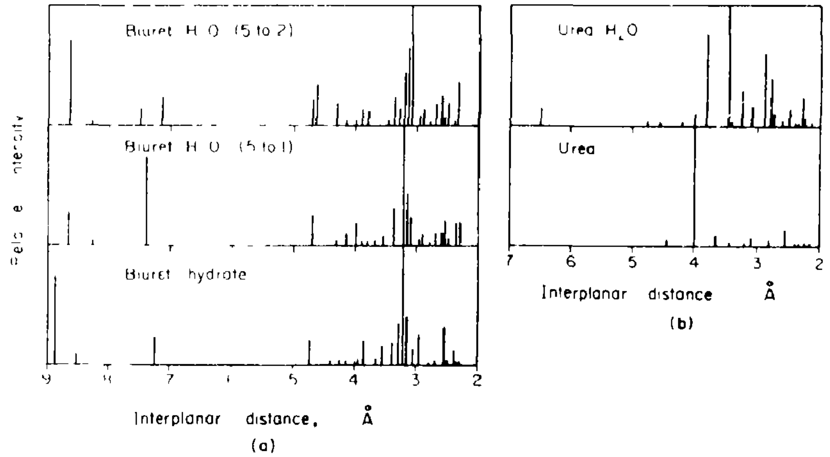


FIG 3 —X-ray diffraction patterns (Debye-Scherrer) of (a), biuret and its hydrogen peroxide complexes, (b), urea and its hydrogen peroxide complex

It is well known that urea forms many inclusion compounds However, the X-ray analysis[(5)] and the infra-red absorption spectrum of the urea-hydrogen peroxide complex shown above indicate that this is not an inclusion compound On the other hand, the infra-red absorption spectra of biuret-hydrogen peroxide complexes suggest that these must be inclusion compounds Chemical analysis also supports this idea, because the compositions of these complexes suggest that five biuret molecules comprise a unit as in the case of the biuret hydrate The latter compound has already been shown to be an inclusion compound[(2)] in which water is a guest molecule

[(10)] P A GIGUERE, *J Chem Phys* **18**, 88 (1950)

In order to support this point, the X-ray diffraction patterns (Debye-Scherrer) of these complexes are compared. As is seen from Fig. 3b, patterns are completely different between urea and its hydrogen peroxide complex. However, the situation is quite different in biuret hydrate and hydrogen peroxide complexes. Especially the (5 to 1) complex gives almost the same pattern with that of the biuret hydrate. Consequently, it can be said that the (5 to 1) complex is certainly an inclusion compound and probably the (5 to 2) complex, too.

The structural unit of the biuret hydrate is given as follows[2]

$$a = 3.63, \quad b = 17.78, \quad c = 9.18\ \text{Å}, \quad \beta = 119^\circ 30'$$

Assuming the same angle β for the biuret-hydrogen peroxide (5 to 1) complex, it is fairly simple to calculate the spacings of net planes. The coincidence between calculated and observed values is good as is shown in Table 4. The structural unit used in this case is

$$a = 3.63, b = 17.26, \quad c = 9.45\ \text{Å}, \quad \beta = 119^\circ 30'$$

TABLE 4. COMPARISON OF CALCULATED AND OBSERVED SPACINGS OF NET PLANES IN BIURET HYDRATE AND IN BIURET HYDROGEN PEROXIDE COMPLEX (Å)

hkl	Biuret hydrate Calc	Biuret hydrate Obs	Biuret hydrogen peroxide Calc	Biuret hydrogen peroxide Obs
0 2 0	8.89	8.85	8.64	8.63
0 1 1	7.28	7.26	7.42	7.42
0 3 1	4.76	4.75	4.71	4.70
0 1 2	3.89	3.87	4.00	4.00
0 2 2	3.64	3.62	3.71	3.71
0 5 0	3.56	3.58	3.45	3.56
0 3 2	3.31	3.38	3.35	3.36
0 5 1	3.25	3.24	3.18	3.19
1 0 0	*3.16*	*3.19*	*3.16*	*3.19*
1 1 0	3.11	3.15	3.11	3.17
0 4 2	2.97	3.00	2.98	3.09
1 2 0	2.98	2.96	2.97	2.98
1 1 1	2.52	2.54	2.53	2.53
1 2 1	2.44	2.42	2.45	2.40
0 4 3	2.28	2.22	2.31	2.31

CONCLUSION

Two complexes of biuret and hydrogen peroxide are found, $(C_2H_5N_3O_2)_5 H_2O_2$ and $(C_2H_5N_3O_2)_5 (H_2O_2)_2$. Biuret molecules in these complexes have the α-form. In the urea–hydrogen peroxide complex, rather strong hydrogen bonds of the —N—H … O type are formed. No such strong bonds are formed in the biuret–hydrogen peroxide complexes. It is concluded that the biuret–hydrogen peroxide complexes are inclusion compounds in which the hydrogen peroxide is a guest molecule.

Acknowledgements—The author is indebted to Professor S. KINUMAKI of this Institute and to Professor R. C. TAYLOR of University of Michigan for their encouragements throughout this work.

J. Inorg. Nucl. Chem. 1963. Vol. 25. pp. 171 to 174. Pergamon Press Ltd. Printed in Northern Ireland

THE PREPARATION AND COLOUR OF TRIS-2,2′-BIPYRIDYL- AND BIS-2,2′,2″-TERPYRIDYLRHODIUM(III) SALTS

C. M. HARRIS and L. D. McKENZIE
Department of Inorganic and General Chemistry, University of New South Wales,
Kensington, N.S.W.

(*Received* 12 *June* 1962)

Abstract—The preparation of the two series of salts [Rh(2,2′-bipyridyl)$_3$]X$_3$ and [Rh(2,2′,2″-terpyridyl)$_2$]X$_3$ (where X = Cl, Br, I, SCN, and ClO$_4$) is described. The colours of these salts are interpreted in terms of charge transfer from the anions to the colourless cations.

THERE is some confusion in the literature about the colour of the trisbipyridylrhodium(III) cation. JAEGER and VAN DIJK[1] prepared this cation as the chloride, and were generally unable to remove, by recrystallization, the small amount of "blood-red substance" which was contaminating their product. More recently, MARTIN and WAIND[2] reported the perchlorate as being pink, and they interpreted its visible absorption spectrum in terms of crystal field theory. As in the case of the 1,10-phenanthroline analogue,[3] however, the pure hydrated tris-bipyridylrhodium(III) chloride can be obtained completely colourless, using activated charcoal to adsorb the coloured impurity. The differential adsorption on charcoal is less marked for the bis-terpyridyl salt, and in this case the percentage recovery of the colourless material from the recrystallization is very low. The absorption spectra of these cations in the ultra-violet region are shown in Fig. 1. For the tris-bipyridyl-complex, the spectrum is in agreement with MARTIN and WAIND's measurement in aqueous solution. Their spectrum in the visible region is doubtless due to the coloured impurity, which, by its close analogy with the phenanthroline analogue[3] appears to be a mono-chelated complex.

A number of salts of these cations have been prepared, and are listed in the Table, together with their colours. The bisterpyridyl compounds are reported for the first time, as are a number of the trisbipyridyl compounds. Their colours increase with increasing polarizability of the anion, and range from colourless for the perchlorate and hydrated chloride, through various shades of yellow, to a deep orange-red for the anhydrous iodide. Such colours are doubtless a result of an interionic charge-transfer process, of the type discussed by ORGEL for the hexamminerhodium(III) halides.[4]

$$[\mathrm{Rh\ bipy_3}]^{3+} + \mathrm{I}^- + h\nu \rightarrow [\mathrm{Rh\ bipy_3}]^{2+} + \mathrm{I}$$

The increase in colour on dehydration, indicating a shift of the absorption to longer wavelength, is a result of the closer approach of the ions lowering the energy required for the charge-transfer process. The flat chelate molecules give the cations a paddle wheel shape, and the water of crystallization is probably located in the angles. Removal of this water thus allows closer approach of the anion to the central metal atom, although it should be noted that the charge transfer may occur through the aromatic ring system of the ligand.

---

[1] F. M. JAEGER and J. A. VAN DIJK, *Kon. Akad. van Wetens., Amsterdam* **37**, 284 (1934).

[2] B. MARTIN and G. M. WAIND, *J. Chem. Soc.* 4284 (1958).

[3] L. D. McKENZIE and R. A. PLOWMAN, Unpublished work (1958).

[4] L. E. ORGEL, *Quart. Rev.* **8**, 422 (1954).

We were interested to see if the anion was sufficiently close to the cation, to give, in effect, a stable seven or eight-covalent species, which would persist in non-aqueous solvents such as nitromethane and nitrobenzene since it was noted that the thiocyanates and iodides gave yellow solutions in these solvents. The observation of charge-transfer bands in the copper complexes Cu chelate$_2$X$_2$ (where chelate = 1,10-phenanthroline and 2,2′-bipyridyl, and X = a univalent anion) led to the demonstration that copper had a coordination number of five in these compounds, with a trigonal bipyramidal stereochemistry.(5) YONEDA's absorption spectral study(6) of the interaction between various anions and the hexamminecobalt(III) and chromium(III) cations, led him to believe that in the association product, the approach of the anion was sufficiently close to give, in effect, a hepta-co-ordinated complex.

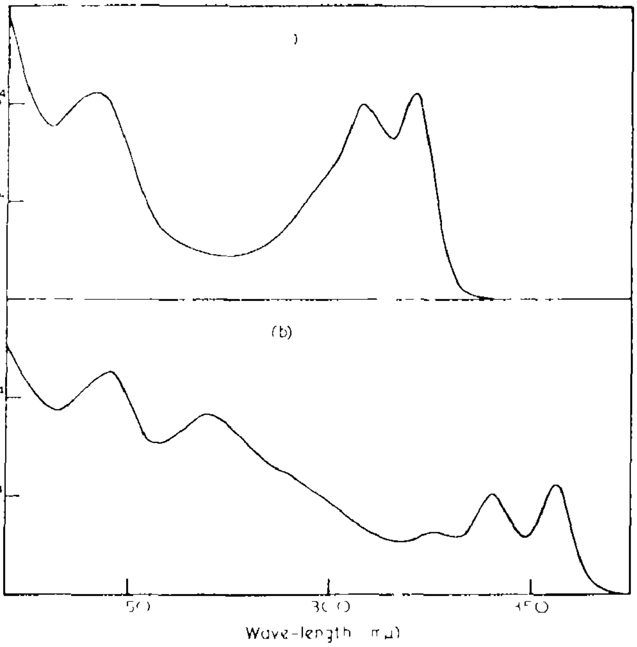


FIG. 1.—Absorption spectra in methanol of (a) 1·6 × 10^{-5} M [Rh bipy$_3$]Cl$_3$·4·5H$_2$O and (b) 1·5 × 10^{-5} M [Rh(terpy)$_2$]Cl$_3$·7H$_2$O. Maxima occur at (a) 242, (300), 308, and 321 mμ, and (b) 246, 270, (290), 326, 341, 356 mμ.

The conductances of the various rhodium salts in nitromethane are listed in the Table, together with those of some simple salts to give a comparison of the mobility of the anions. These indicate that, although there may be some association, increasing in the order $I^- < SCN^- < Br^- < Cl^-$, it is not sufficient to indicate the existence of a significant concentration of a stable species of higher co-ordination number. Even in the more weakly polar solvent nitrobenzene, a conductometric titration of tris-bipyridylrhodium(III) perchlorate with triphenylmethylarsonium iodide gave a straight line plot. It is pertinent to note that a recent study of aqueous copper(II) bromide has shown that the concentration of the $CuBr^{+}$ species, which is responsible for a charge transfer band at 280 mμ, is so small as to be "scarcely detectable by measurements of thermodynamic properties or conductances"(7). The intensity of the charge transfer bands is such that the species responsible for them need be present in only very small concentration.

---

(5) C. M. HARRIS, T. N. LOCKYER and H. WATERMAN, *Nature, Lond.* **192**, 424 (1961). G. A. BARCLAY and C. H. L. KENNARD, *Nature, Lond.* **192**, 425 (1961).

(6) H. YONEDA, *Bull. Chem. Soc., Japan* **28**, 125 (1955).

TABLE 1.—MOLECULAR CONDUCTANCES IN NITROMETHANE AT 25.0°C

Compound	Colour	Concentration	Conductance (mho)
$[Rh\ bipy_3]Cl_3 \cdot 4.5H_2O$	Colourless: pale yellow when anhydrous	0.92×10^{-3} M	230
$[Rh\ bipy_3]Br_3 \cdot 4.5H_2O$	Colourless: yellow when anhydrous	0.73×10^{-3} M	240
$[Rh\ bipy_3](SCN)_3 \cdot 3H_2O$	Yellow: bright yellow when anhydrous	0.91×10^{-3} M	248
$[Rh\ bipy_3]I_3 \cdot 3H_2O$	Bright yellow—orange when anhydrous and red on heating	0.67×10^{-3} M	251
$[Rh\ bipy_3](ClO_4)_3 \cdot 3.5H_2O$	Colourless	0.92×10^{-3} M	261
$[Rh\ terpy_2]Cl_3 \cdot 7H_2O$	Colourless: yellow when anhydrous	0.49×10^{-3} M	254
$[Rh\ terpy_2]Br_3 \cdot 6H_2O$	Pale cream—yellow when anhydrous	0.63×10^{-3} M	238
$[Rh\ terpy_2](SCN)_3 \cdot 4H_2O$	Yellow—yellow when anhydrous	Insoluble	—
$[Rh\ terpy_2]I_3 \cdot 2H_2O$	Orange—Orange-red when anhydrous	0.65×10^{-3} M	251
$[Rh\ terpy_2](ClO_4)_3 \cdot 2H_2O$	Colourless	1.08×10^{-3} M	252
NEt_4Br		1.45×10^{-3} M	103
NEt_4I		1.35×10^{-3} M	103
NEt_4ClO_4		1.48×10^{-3} M	104

EXPERIMENTAL

Preparation of compounds

$[Rh\ bipy_3]Cl_3 \cdot 4.5H_2O$ *and* $[Rh\ bipy_3]Br_3 \cdot 4.5H_2O$.* Rhodium(III) chloride or rhodium(III) bromide was fused with bipyridyl (in the ratio 1 : 3.5) and the melt boiled 10 min. Aqueous ethanol (50 per cent) was then added dropwise and the resulting solution refluxed for several hours. It was then treated with animal charcoal and refluxed for a further 30 min, after which the product was precipitated from the filtered solution by the addition of acetone. The colourless crystalline product was filtered off, washed with acetone, and dried in air. (Found: Rh, 13.5; C, 47.2; H, 4.4; N, 11.1. Calc. for $C_{30}H_{33}Cl_3N_6O_{4.5}Rh$: Rh, 13.6; C, 47.5; H, 4.4; N, 11.1%. Found: Rh, 11.6; C, 40.1; H, [illegible]6; N, 9.4. Calc. for $C_{30}H_{33}Br_3N_6O_{4.5}Rh$: Rh, 11.6; C, 40.4; H, 3.7; N, 9.4%.)

$[Rh\ bipy_3](SCN)_3 \cdot 3H_2O$. The compound was precipitated from an ethanol solution of the chloride with lithium thiocyanate. (Found: C, 49.9; H, 3.7; N, 15.4. Calc. for $C_{33}H_{30}N_9O_3RhS_3$: C, 49.6; H, 3.75; N, 15.8%.)

$[Rh\ bipy_3]I_3 \cdot 3H_2O$. The compound was precipitated from an aqueous ethanol (20 : 80) solution of the chloride with lithium iodide. (Found: Rh, 10.2; C, 35.7; H, 3.2; N, 8.3; H_2O, 5.2. Calc. for $C_{30}H_{30}I_3N_6O_3Rh$: Rh, 10.2; C, 35.8; H, 3.0; N, 8.35; H_2O, 5.4%.)

---

* The essential features of this method were designed by Jaeger and Van Dijk.

(7) D. A. I. HOPE, R. J. OTTER and J. E. PRUE, *J. Chem. Soc.* 5226 (1960).

$[Rh\,bipy_3](ClO_4)_3 \cdot 3.5H_2O$. The compound was precipitated from an aqueous solutions of the chloride with sodium perchlorate. (Found: C, 38.8; H, 3.5; N, 8.6. Calc. for $C_{30}H_{31}Cl_3N_6O_{15.5}Rh$: C, 38.7; H, 3.3; N, 9.0%.)

$[Rh\,terpy_2]Cl_3 \cdot 7H_2O$ *and* $[Rh\,terpy_2]Br_3 \cdot 6H_2O$. The method was the same as for the bipyridyl compounds except that several treatments with animal charcoal were necessary before a colourless product was obtained, and the percentage recovery was small. (Found: Rh, 13.0; C, 44.4; H, 4.5; N, 11.2. Calc. for $C_{30}H_{36}Cl_3N_6O_7Rh$: Rh, 12.8; C, 44.9; H, 4.5; N, 10.5%. Found: Rh, 11.3; C, 39.0; H, 3.9; N, 8.9. Calc. for $C_{30}H_{34}Br_3N_6O_6Rh$: Rh, 11.2; C, 39.3; H, 3.7; N, 9.2%.)

$[Rh\,terpy_2](SCN)_3 \cdot 4H_2O$. As for the bipyridyl compound. (Found: C, 48.0; H, 3.1; N, 15.8. Calc. for $C_{33}H_{30}N_9O_4RhS_3$: C, 48.6; H, 3.7; N, 15.5%.)

$[Rh\,terpy_2]I_3 \cdot 2H_2O$. The compound was precipitated from an ethanol solution of the bromide with lithium iodide. (Found: C, 36.8; H, 2.9; N, 8.6. Calc. for $C_{30}H_{26}I_3N_6O_2Rh$: C, 36.5; H, 2.7; N, 8.5%.)

$[Rh\,terpy_2](ClO_4)_3 \cdot 2H_2O$. As for the bipyridyl compound. (Found: C, 40.5; H, 3.1; N, 7.8. Calc. for $C_{30}H_{26}Cl_3N_6O_{14}Rh$: C, 40.0; H, 2.7; N, 9.3%.)

Absorption spectra and conductance measurements

The spectra were obtained on a Cary Spectrophotometer model MS11, using 1 cm Silica cells and 2×10^{-3} M solutions in methanol.

The conductance measurements in freshly distilled nitromethane were obtained with a Phillips Conductivity Bridge model GM4249 and a dip type cell model GM4221/01.

Acknowledgement. The authors are indebted to Dr E. CHALLEN for the semi-microanalyses of carbon, hydrogen and nitrogen.

J. Inorg. Nucl. Chem. 1963, Vol. 25, pp. 175 to 178. Pergamon Press Ltd. Printed in Northern Ireland

SOME REACTIONS OF TETRA(DIMETHYLAMINO)-DIBORON

A. G. MASSEY and N. R. THOMPSON
University Chemical Laboratory, Lensfield Road, Cambridge

(Received 22 June 1962; in revised form 16 July 1962)

Abstract—The reactions of tetra(dimethylamino)diboron, $B_2[N(CH_3)_2]_4$, with oxygen, hydrogen, ethylene, nitric oxide and various chlorinating and fluorinating agents are described.

DIBORON compounds, as simple sources of boron-boron bonds, have received active interest in the last two decades.[1] The halides are difficult to prepare but recently it has proved possible to isolate tetra(dimethylamino)diboron, $B_2[N(CH_3)_2]_4$, in high yield by the Wurtz-type reaction.[2]

$$2XB[N(CH_3)_2]_2 + 2Na \rightarrow 2NaX + B_2[N(CH_3)_2]_4$$

X = Chlorine or bromine

Tetra(dimethylamino)diboron, a colourless, slightly volatile liquid, is extremely sensitive to traces of moisture with which it produces dimethylamine and sub-boric acid. Previous workers had noted its high thermal stability; we restudied the thermal decomposition hoping to prepare such compounds as $[BN(CH_3)_2]_x$ analogous to the boron chlorides B_4Cl_4, B_8Cl_8 and $(BCl)_x$.

$$xB_2[N(CH_3)_2]_4 \rightarrow xB[N(CH_3)_2]_3 + [BN(CH_3)_2]_x$$

Table 1 shows that even after many days at 300° only about 20 per cent of the boron-boron bonds had been broken. The decomposition, though producing tri(dimethylamino)borane, $B[N(CH_3)_2]_3$, as one product was obviously not straight-forward since methane was obtained in significant yield indicating parallel fission of the carbon–nitrogen bonds. Furthermore, infra-red studies on the liquid product also indicated traces of a compound containing boron hydrogen links although the yield of this compound was so small as to preclude its isolation. (Its presence will of course affect

TABLE 1.—THERMAL DECOMPOSITION OF TETRA(DIMETHYLAMINO)DIBORON
(Quantities expressed in mmoles)

Experiment No.	1	2	3	4
$B_2(NMe_2)_4$ used	0.84	0.92	0.84	0.92
Temperature (°C)	200	300	300	300
Time (days)	4	4	16	24
Hydrogen removed	0.01	0.06	trace	0.00
Methane removed		0.01	0.12	0.17
Dimethylamine removed	0.03	0.11	0.03	0.02
Hydrogen on alkaline hydrolysis of liquid residue	0.76	0.76	0.67	-
Recovery of B–B bonds (%)	92	83	80	

---

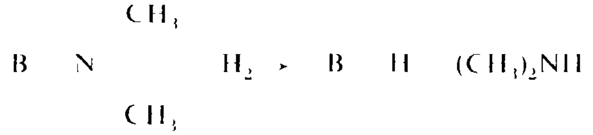
[1] A. K. HOLLIDAY and A. G. MASSEY, *Chem. Revs.* **62** (1962).
[2] R. J. BROTHERTON, A. L. MCCLOSKEY and H. STEINBERG, *J. Amer. Chem. Soc.* **82**, 6242 (1960).

the estimation, by alkaline hydrolysis, of boron boron bonds in the decomposition products though to a negligible extent)

It has been reported that tetra(dimethylamino)diboron is not attacked by oxygen[2], but on repeating the work under more quantitative and more vigorous conditions we found a complex reaction In some experiments dimethylaminoboroxole, $[BON(CH_3)_2]_3$ and tri(dimethylamino)borane were formed as might be expected from previous work using the tetra-alkoxydiborons[3]

$$B_2[N(CH_3)_2]_4 + \tfrac{1}{2}O_2 \rightarrow B[N(CH_3)_2]_3 + \tfrac{1}{3}[BON(CH_3)_2]_3$$

However only when the tetra(dimethylamino)diboron was in a large excess (Expt 8, Table 2) were reaction ratios obtained which approximated to those demanded by the equation but even then side reactions also produced methane, hydrogen and dimethylamine Though the simultaneous presence of amines and carbon dioxide in some experiments caused difficulty in obtaining accurate volume data the results clearly showed amounts of free amine which could not be explained away by adventitious hydrolysis of the starting material by water occluded in the glass walls of the reaction vessel cf the small amounts of amine isolated in the decomposition experiments The presence of hydrogen in the gaseous products suggested the amine may have arisen from a reaction of the type



$$B-N(CH_3)_2 + H_2 \rightarrow B-H + (CH_3)_2NH$$

but subsequent experiments showed hydrogen did not react with tetra(dimethylamino)diboron under these conditions cf the reaction of diboron tetrachloride and hydrogen[1] The reaction products carbon monoxide and carbon dioxide indicated that oxidation of the organic material was taking place

$$CH_3 + O_2 \rightarrow CO + CO_2 + H_2O$$

Water formed in this way would certainly explain the isolation of dimethylamine

$$B-N(CH_3)_2 + H_2O \rightarrow B-OH + HN(CH_3)_2$$

but the mechanism by which ammonia and mono-methylamine appear as products remains obscure

Other diboron compounds show remarkable activity towards nitric oxide[1] However tetra(dimethylamino)diboron reacted only sluggishly, and incompletely, at 200° to produce nitrous oxide, dimethylamino boroxole and tri(dimethylamino)borane presumably according to the equation

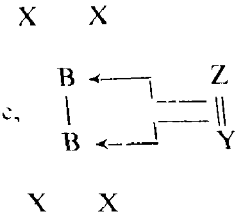
$$B_2[N(CH_3)_2]_4 + 2NO \rightarrow N_2O + \tfrac{1}{3}[BON(CH_3)_2]_3 + B[N(CH_3)_2]_3$$

The incompleteness of the reaction and the extreme volatility of the nitric oxide precluded a quantitative study of the system

Ethylene reacts smoothly at low temperatures with the diboron tetrahalides[1] to produce 1,2 bis(dihaloboryl)ethanes, $X_2BC_2H_4BX_2$, X = Cl or I Ethylene did not react with tetra(dimethylamino)diboron at 200°, nor did the two react at room temperature in the presence of boron trichloride The decreased reactivity of tetra(dimethylamino)diboron towards the π-bonded donor molecules oxygen, nitric oxide and ethylene (as compared to the diboron halides) is no doubt due to substantial "back-donation" of electrons from the nitrogen atoms into the vacant 2*p*-orbitals of the two boron atoms Such an effect would inhibit a reaction involving an intermediate of the

---

[3] R J Brotherton A L McCloskey, J L Boone and H M Manasevit, *J Amer Chem Soc* 82, 6245 (1960)

type,  , postulated to occur in the reactions of ethylene, oxygen and

nitric oxide with diboron tetrachloride [1]

The attempted fluorination or chlorination of tetra(dimethylamino)diboron using phosphorus (III) chloride, antimony (III) fluoride, iodine pentafluoride and tin (IV) chloride gave involatile moisture sensitive solids and liquids but no volatile compounds When excess of sulphur chloride pentafluoride, SF_5Cl was used boron trifluoride was produced, chlorine and sulphur tetrafluoride being isolated as by-products

Although transamination reactions occur with several amines including monoethylamine,[2] little or no exchange occurred between tetra(dimethylamino)diboron and ammonia even at room temperature thus allowing studies to be made on the diboron compound in liquid ammonia However, the hope that useful substitution reagents, such as $KB[N(CH_3)_2]_3$, might be made was short-lived, potassium or sodium did not cleave the boron boron bond in liquid ammonia 78°

EXPERIMENTAL

Volatile compounds were handled in conventional vacuum systems products which were moisture sensitive were handled in a dry-box Quantities given below are expressed in mmoles unless otherwise stated

We thank Borax Consolidated Ltd for the sample of tetra(dimethylamino)diboron On hydrolysis with 10 per cent caustic soda at 100 235.1 mg of the tetra(dimethylamino)diboron (1.188) produced 1.036 mmole of hydrogen in 5.5 hr, 1.182 mmole in 10.5 hr and 1.188 mmole at the end of 15.5 hr

Hydrolysis of the tetra(dimethylamino)diboron sometimes produced small amounts of ammonia mixed with the dimethylamine the infra-red spectrum of tetra(dimethylamino)diboron showed no N H bonds whilst analysis showed its purity approached 100 per cent A further unexplained fact noted in the hydrolysis was that more vigorous conditions (15 hr at 100 120) were required to produce the quantitative amount of hydrogen on fission of the boron boron bond with 10 per cent caustic soda when compared to diboron tetrachloride, which required 3 hr at 70 Both compounds initially produce sub-boric acid which is then oxidised to boric acid

$$B_2(OH)_4 + 2H_2O \xrightarrow{OH^-} 2B(OH)_3 + H_2$$

Reaction with hydrogen

Tetra(dimethylamino)diboron (0.71) and hydrogen (1.29) were heated in a sealed tube at 200 for 48 hr The volatile products were hydrogen (1.30) and dimethylamine (0.04) An infra-red study of the remaining liquid showed it to be pure tetra(dimethylamino)diboron

Reaction with oxygen

The experiments, conducted at 200-300 in sealed tubes, are summarized in Table 2 Combustion and infra-red analyses showed the non-condensable products to be hydrogen methane and sometimes, carbon monoxide The material volatile at 78 was mainly dimethylamine varying proportions of monomethylamine and ammonia were also present. If a large excess of oxygen was used (Experiments 12 and 13) carbon dioxide and nitrous oxide could also be detected in the −78° volatile fraction.

When oxygen : tetra(dimethylamino)diboron ratios of about 1 : 1 were used, large colourless crystals identified by their volatility and infra-red spectrum as dimethylamino boroxole $[BON(CH_3)_2]_3$, formed on cooling the tubes to room temperature; infra-red spectra of the liquid residues also revealed the presence of tri(dimethylamino)borane. Reaction ratios greater than 1 : 1 produced non-volatile tar-like materials indicating extensive oxidation of the organic material.

TABLE 2. REACTION OF TETRA(DIMETHYLAMINO)DIBORON WITH OXYGEN
(Quantities expressed in mmoles)

Experiment No.	5	6	7	8	9	10	11	12	13
$B_2[N(CH_3)_2]_4$ taken	0.59	1.03	0.83	1.39	1.08	0.92	0.66	0.44	0.36
Temperature (°C)	200	200	200	300	300	300	300	300	200
Time (days)	3	4	16	1	1	1	6	1	10
Oxygen added	1.13	0.90	1.06	0.45	0.83	1.03	1.25	2.19	1.94
Oxygen recovered	0.74	0.00	0.00	0.00	0.00	0.00	0.00	0.25	0.15
Non-condensable gas removed	0.00	0.04	0.08	0.11	0.13	0.06	0.13	0.38	0.19
−78° Volatile material removed	0.36		1.30	--	1.18	–	1.19	0.95	0.43
Hydrogen on alkaline hydrolysis of liquid residues	0.00	0.00		0.61	0.00	0.00	0.00	0.00	
Ratio $O_2 : B_2[N(CH_3)_2]_4$	0.66 : 1	0.87 : 1	1.3 : 1	0.58 : 1	0.77 : 1	1.1 : 1	1.9 : 1	4.0 : 1	5.0 : 1

Reaction with nitric oxide

Tetra(dimethylamino)diboron (0.86) and nitric oxide (1.01) were held at 200° for 48 hr. Nitric and nitrous oxides (0.86) were recovered; alkaline hydrolysis of the liquid residue indicated that 0.65 mmoles of tetra(dimethylamino)diboron remained unchanged. Other similar experiments showed the presence of small amounts of dimethylaminoboroxole and tri(dimethylamino)borane in the reaction products.

Reaction with ethylene

Ethylene was recovered in over 99 per cent yield when heated with tetra(dimethylamino)diboron at 200° for 48 hr; no ethylene take-up was detected when the two were held at room temperature in the presence of boron trichloride for three days.

Reaction with ammonia

Tetra(dimethylamino) diboron (1.00) and ammonia (7.32) were held at room temperature for ten days in a sealed tube. At the end of this time 7.36 mmole of ammonia, containing only a trace of dimethylamine, were recovered. Micro- and infra-red analyses of the remaining liquid residue showed it to be unchanged tetra(dimethylamino)diboron.

Reaction with sulphur chloride pentafluoride

Sulphur chloride pentafluoride (0.70) and tetra(dimethylamino)diboron (1.14) were allowed to warm up slowly from −196°. Just below room temperature a vigorous reaction produced an involatile liquid and a little thionyl fluoride, SOF_2. Alkaline hydrolysis at 100° for 10 hr produced 0.32 mmole of hydrogen showing that extensive cleavage of the boron–boron bond had occurred. Experiments conducted at room temperature with an excess of sulphur chloride pentafluoride produced boron trifluoride, sulphur tetrafluoride and chlorine as the products volatile at −112°, traces of sulphur dioxide where retained by the −112° trap. The involatile liquid residues contained no boron–boron bonds. The lack of boron trichloride in the volatile products prompted a study of the system, boron trichloride–sulphur chloride pentafluoride; no reaction occurred at room temperature.

Acknowledgement—We thank the Imperial Chemical Industries and British Titan Products for Fellowships.

J Inorg Nucl Chem 1963 Vol 25 pp 179 to 185 Pergamon Press Ltd Printed in Northern Ireland

SYNTHESIS AND ALKYLATION OF $[Fe(CN)_2(C_5H_5)(CO)]^-$, $[Mo(CN)_2(C_5H_5)(CO)_2]^-$, $[W(CN)_2(C_5H_5)(CO)_2]^-$ and $[W(CN)(C_5H_5)(CO)_3]$

C Eugene Coffey
Explosives Dept, E I du Pont de Nemours & Co, Wilmington, Delaware

Abstract—$[Fe(CN)_2(C_5H_5)(CO)]^-$ was best prepared by reacting $[FeBr(C_5H_5)(CO)_2]$ with potassium cyanide in aqueous ethanol Two other syntheses were also found Alkylation of the anion with alkyl halides gave two series of isocyanide complexes neutral $[Fe(CN)(C_5H_5)(CO)(CNR)]$ and cationic $[Fe(C_5H_5)(CO)(CNR)]^+$ The reaction of potassium cyanide with $[WCl(C_5H_5)(CO)_3]$ gave $[W(CN)(C_5H_5)(CO)_3]$ and $K[W(CN)_2(C_5H_5)(CO)_2]$, $[MoCl(C_5H_5)(CO)_3]$ gave only $K[Mo(CN)_2(C_5H_5)(CO)_2]$ Alkylation of the tungsten monocyanide complex with methyl iodide gave the isocyanide complex $[W(C_5H_5)(CO)_3(CNCH_3)]I$ and alkylation of the molybdenum dicyanide complex gave $[Mo(C_5H_5)(CO)_2(CNCH_3)_2]I$ Attempts to form other cyclopentadienyl-carbonyl-cyanide complexes were unsuccessful

The union of metal carbonyl with arene-metal chemistry has produced a fertile area of mixed ligand chemistry [(1)] However, little attention has been given to arene-carbonyl complexes in which one or more carbonyl ligands are replaced by carbonyl-like ligands In particular, no arene-carbonyl-isocyanide complexes and only one arene-carbonyl-cyanide complex[(2)] have appeared in the literature

This paper reports the synthesis of four cyclopentadienyl-carbonyl-cyanide complexes of iron, molybdenum and tungsten and the alkylation of these complexes to isocyanide complexes of two kinds

RESULTS

Cyano-cyclopentadienyl-carbonyl complexes Potassium dicyanocyclopentadienylcarbonyliron(II) was best obtained through the reaction of potassium cyanide with bromocyclopentadienyldicarbonyliron(II)[(3)] in aqueous ethanol according to (1) The

$$[FeBr(C_5H_5)(CO)_2] + 2KCN \rightarrow K[Fe(CN)_2(C_5H_5)(CO)] + CO + KBr \qquad (1)$$

complex also resulted from the oxidation of $K_2[Fe(CN)_2(C_5H_5)(CO)]$[(4)] with bromine A third route was afforded by the reaction of potassium cyanide with cyclopentadienyldicarbonylironchloromercurate(II)[(5)] as shown in (2)

$$HgCl[Fe(C_5H_5)(CO)_2] + 2KCN \rightarrow K[Fe(CN)_2(C_5H_5)(CO)] + Hg + CO + KCl \quad (2)$$

The potassium salt of the complex is stable in air very soluble in water and sparingly soluble in polar organic solvents Aqueous solutions of the complex gave insoluble precipitates with silver nitrate, mercuric chloride and dimethyltin dichloride

---

(1) Two recent reviews discuss arene-metal complexes (a) G Wilkinson and F A Cotton in *Progress in Inorganic Chemistry* (Edited by F A Cotton) Interscience New York (1959) pp 1 124 and (b) E O Fischer and H P Fritz in *Advances in Inorganic Chemistry and Radiochemistry* (Edited by H J Emeleus and A G Sharpe) pp 55–115 Academic Press New York (1959)

(2) T S Piper and G Wilkinson, *J Inorg Nucl Chem* **3**, 104 (1956)

(3) B F Hallam, O. S Mills and P L Pauson, *J Inorg Nucl Chem* **1**, 313 (1955)

(4) J C Thomas Unpublished work

(5) J C Thomas, *U S Pat* 2849471

Acidification of aqueous solutions of the complex precipitated the somewhat air-sensitive parent acid $H[Fe(CN)_2(C_5H_5)(CO)]$ The ammonium salt of the complex was prepared by passing anhydrous ammonia into a solution of the complex in ethanol

Potassium cyanide reacted with an equimolar quantity of $[WCl(C_5H_5)(CO)_3]$ in aqueous methanol to produce the monocyanide complex as shown in (3) The

$$[WCl(C_5H_5)(CO)_3] + KCN \rightarrow [W(CN)(C_5H_5)(CO)_3] + KCl \qquad (3)$$

corresponding molybdenum monocyanide complex could not be isolated from the *products of the reaction of $[MoCl(C_5H_5)(CO)_3]$*(2) with potassium cyanide However with two moles of potassium cyanide the chloro complexes of both tungsten and molybdenum reacted as shown in (4)

$$[MCl(C_5H_5)(CO)_3] + 2KCN \rightarrow K[M(CN)_2(C_5H_5)(CO)_2] + KCl + CO \qquad (4)$$

The tungsten monocyanide complex was photo-sensitive but stable to air and water It was shown to be monomeric in benzene and a non-electrolyte in nitrobenzene Both the molybdenum and tungsten dicyanide complexes were obtained as very hygroscopic yellow powders which were difficult to free of solvent Their identification rests on the infrared spectra and the conversion of the molybdenum complex to an isocyanide derivative (below) which was easily characterized

Although $[Co(C_5H_5)(CO)_2]$(6) was readily attacked by potassium cyanide, apparently producing $K[Co(CN)(C_5H_5)(CO)]$, we were unable to isolate the product in a pure state Surprisingly the complexes $[Mn(CH_3C_5H_4)(CO)_3]$ and $[Cr(CO)_3(\text{mesitylene})]$(7) were not attacked by potassium cyanide in refluxing aqueous ethanol

Alkylation reactions Alkylation of $K[Fe(CN)_2(C_5H_5)(CO)]$ was carried out with a variety of alkyl bromides and iodides Alkyl chlorides reacted too slowly to make the reaction practical and aromatic halides did not react at all Alkylation of the tungsten and molybdenum complexes was attempted only with methyl iodide

Refluxing the complex iron salt for several hours in acetronitrile with an equimolar quantity of alkyl halide gave monoisocyanide complexes according to (5) This

$$K[Fe(CN)_2(C_5H_5)(CO)] + RX \rightarrow [Fe(CN)(C_5H_5)(CO)(CNR)] + KX \qquad (5)$$

reaction was carried out with R = allyl, benzyl, *p*-chlorobenzyl, *p*-carbethoxybenzyl and triphenyl-methyl These isocyanide complexes were insoluble in water but soluble in organic solvents Air oxidation of the complexes occurred over a period of days but the complexes were immediately decomposed in solution by base, and cyanide ion in particular, with liberation of free isocyanide

Alkylation of the iron complex in acetonitrile with excess alkyl halide gave cationic diisocyanide complexes as shown in (6) Complexes were obtained with R = methyl,

$$K[Fe(CN)_2(C_5H_5)(CO)] + 2RX \rightarrow [Fe(C_5H_5)(CO)(CNR)_2]X + KX \qquad (6)$$

allyl and benzyl These ionic complexes were soluble in water and polar organic solvents and had about the same stability to air and bases as the monoisocyanide complexes The methyl and benzyl complexes had conductivities in water and nitrobenzene which were consistent with the proposed ionic structure

---

(6) T S Piper, F A Cotton and G Wilkinson, *J Inorg Nucl Chem* **1**, 165 (1955)

(7) B Nicholls and M C Whiting, *Proc Chem Soc* 152 (1958)

The tungsten complex $[W(CN)(C_5H_5)(CO)_3]$ was methylated by methyl iodide in acetonitrile to give $[W(CNCH_3)(C_5H_5)(CO)_3]^+I^-$ as a water soluble, photosensitive solid Attempts to alkylate $K[W(CN)_2(C_5H_5)(CO)_2]$ were unsuccessful but $K[Mo(CN)_2(C_5H_5)(CO)_2]$ was easily methylated to $[Mo(C_5H_5)(CO)_2(CNCH_3)_2]I$ The molybdenum and tungsten isocyanide complexes were stable to air but rapidly decomposed in solution by bases

DISCUSSION

Two cyclopentadienyl–cyanide complexes were known prior to this work PIPER and WILKINSON(2) made $[Fe(CN)(C_5H_5)(CO)_2]$ by treating $[FeBr(C_5H_5)(CO)_2]$ with potassium cyanide in ethanol and THOMAS(4) prepared the monovalent iron complex, $K_2[Fe(CN)_2(C_5H_5)(CO)]$, by the reaction of potassium cyanide with $[Fe(C_5H_5)(CO)_2]_2$ No cyclopentadienyl isocyanide complexes have been reported in the literature

The attack of cyanide ion on $[FeBr(C_5H_5)(CO)_2]$ displayed an interesting specificity In ethanol cyanide ion displaced the bromide ion exclusively and the resulting uncharged complex was inert to (or reacted very slowly with) cyanide ion In 50 per cent aqueous ethanol, however, both the bromide and one carbon monoxide were displaced, giving a negatively charged dicyano complex The latter complex was only slightly decomposed (to ferricyanide) by treatment with aqueous potassium cyanide at 200 for 2 hr This extreme resistance to attack by cyanide ion can only be partially explained as a consequence of electrostatic repulsion between the two negatively charged reactants, the reaction of CN with $[Cu(CN)_2]$ for example proceeds rapidly Possibly the explanation lies in the relative π-acceptor capabilities of CO and CN^- The cyanide ligand is a less effective π-acceptor than CO and thus will tend to increase the negative charge on iron and increase the amount of π-bonding from iron to CO Both effects would oppose displacement of the last CO by CN

The alkylation of cyanide complexes by alkyl halides is a well-known route to isocyanide complexes(8) and has been of recent interest in this larobatory (9 10) Alkylation of $[Fe(CN)_2(C_5H_5)(CO)]$ proceeded readily and gave two series of complexes, neutral $[Fe(CN)(C_5H_5)(CO)(CNR)]$ and cationic $[Fe(C_5H_5)(CO)(CNR)_2]$ Methylation of $[W(CN)(C_5H_5)(CO)_3]$ and $[Mo(CN)_2(C_5H_5)(CO)_2]^-$ was carried out without difficulty Surprisingly, we were unable to methylate $[W(CN)_2(C_5H_5)(CO)_2]^-$ (The reaction mixture contained $[W(C_5H_5)(CO)_3(CNCH_3)]I$, starting material and decomposition products) The isocyanide complexes prepared in this work are unique in having both cyclopentadienyl and isocyanide ligands attached to the central metal ion and the isocyanide complexes of tungsten and molybdenum appear to be the first divalent isocyanide complexes of these metals

The complexes $[Fe(CN)(C_5H_5)(CO)(CNR)]$ are interesting in that all four ligands attached to iron are different It follows that these complexes must exist as enantiomorphic pairs unless all of the metal–ligand bonds are coplanar No attempt was made to separate optical isomers in this work, but one of the complexes described below, $[Fe(CN)(C_5H_5)(CO)(CNCH_2C_6H_4COOH)]$, should be capable of resolution through salt formation with an optically active base.

---

(8) A comprehensive review of metal isocyanide complexes is given by L MALATESTA in *Progress in Inorganic Chemistry*, (Edited by F A COTTON) pp 283–379 Interscience New York (1959)

(9) W Z HELDT In press Presented in part at the sixth International Conference on Co-ordination Chemistry, held at Wayne State University, Detroit Michigan August, 1961

(10) J A C ALLISON Unpublished work

Infra-red spectra of the iron complexes provided a clear delineation between the three types of complex: anionic, neutral monoalkylated and cationic dialkylated. Bands observed in the 2000 cm^{-1} region are given in Table 1. The characteristic bands of terminal metal carbonyl, cyanide and isocyanide ligands fell in rather narrow and non-overlapping regions of the spectrum. (The splitting of the metal carbonyl band in $K[Fe(CN)_2(C_5H_5)(CO)]$ must arise from crystal effects.) Infra-red spectra of the molybdenum and tungsten complexes are described in the Experimental section.

TABLE 1.* INFRA-RED BANDS (cm^{-1}) IN 2000 cm^{-1} REGION

Complex	CO	CN	CNR
Anionic			
$K[Fe(CN)_2(C_5H_5)(CO)]$	1950, 1970	2080	
$H[Fe(CN)_2(C_5H_5)(CO)]$	1990	2100, 2135	
Neutral			
$[Fe(CN)(C_5H_5)(CO)(CNCH_2CH{=}CH_2)]$†	1970	2090	2170
$[Fe(CN)(C_5H_5)(CO(CNCH_2C_6H_5)]$†	1980	2100	2185
$[Fe(CN)(C_5H_5)(CO(CNCH_2C_6H_4Cl)]$	2000	2115	2205
$[Fe(CN)(C_5H_5)(CO)(CNCH_2C_6H_4COOC_2H_5)]$	1975	2105	2200
$[Fe(CN)(C_5H_5)(CO)(CNCH_2C_6H_4COOH)]$	1990	2110	2180
$[Fe(CN)(C_5H_5)(CO)(CNC(C_6H_5)_3)]$	1990	2090	2140
Cationic			
$[Fe(C_5H_5)(CO)(CNCH_3)_2]I$	2000		2200
$[Fe(C_5H_5)(CO)(CNCH_2CH{=}CH_2)_2]Br$	2010		2200
$[Fe(C_5H_5)(CO)(CNCH_2C_6H_5)_2]Br$	2010		2200

* Spectra were taken in KBr disc except where noted.
† Spectrum of thin film of oil between KBr plates.

EXPERIMENTAL

All materials were commercially available unless otherwise noted. Infra-red spectra were recorded on a Perkin-Elmer "Infracord".

Potassium Dicyanocyclopentadienylcarbonylferrate (II). A cooled mixture of 35.4 g (0.100 mole) of $[Fe(C_5H_5)(CO)_2]_2$(11) in 250 ml of methanol was treated dropwise with 16.0 g (0.100 mole) of bromine. The resulting solution of $[FeBr(C_5H_5)(CO)_2]$ was warmed to room temperature, a solution of 50 g (0.77 mole) of potassium cyanide in 250 ml of water was added and the mixture was heated at reflux for 0.5 hr. The cooled mixture was filtered and the filtrate evaporated to dryness at reduced pressure. Extraction of the residue with 300 ml of hot ethanol and addition of a large excess of ether to the solution gave 30–50 g of brown-yellow powder which still contained some potassium cyanide.

Recrystallization of a sample of the powder from ethanol gave golden brown crystals soluble in water and insoluble in chloroform. The solid complex was stable in air for weeks, but in hot solution it was noticeably oxidized in a few minutes. (Found: C, 40.6; H, 2.12; N, 11.85. Calcd. for $C_8H_5N_2OFeK$: C, 40.0; H, 2.10; N, 11.68%.)

This complex was also made by the following method. A mixture of 14.2 (0.040 mole) of $[Fe(C_5H_5)(CO)_2]_2$ and 20.8 g (0.32 mole, 100 per cent excess) of potassium cyanide in 300 ml of methanol was refluxed for 15 min and then cooled and a solution of 6.4 g (0.040 mole) of bromine in 50 ml of methanol was added dropwise. The mixture was stirred for 15 min and then filtered and the filtrate evaporated at reduced pressure. Extraction of the residue with hot ethanol and addition of excess ether gave a 45 per cent yield of the crude complex.

---

(11) W. E. CATLIN and J. C. THOMAS, *U.S. Pat.* 2810736.

The complex also resulted from reaction (2) A mixture of 11 55 g (0 028 mole) of $HgCl[Fe(C_5H_5)(CO)_2]$ and 8 g of potassium cyanide in 150 ml of 1 1 ethanol-water solvent was refluxed for 0 5 hr During the reflux period, the complex slowly dissolved and gave a red-brown solution The cooled solution was filtered to remove 5 40 g (94 per cent of theory) of mercury Isolation of the complex as in the preceding examples gave a 65% yield of crude complex

Hydrogen dicyanocyclopentadienylcarbonylferrate (II) Addition of concentrated hydrochloric acid to a cooled, filtered, aqueous solution of $K[Fe(CN)_2(C_5H_5)(CO)]$ precipitated the complex acid as a yellow microcrystalline powder Recrystallization from ethanol–ether gave dark yellow needles which darkened somewhat but did not melt at 250 (Found C, 47 64, H, 3 33, N 13 41 Calcd for $C_8H_6N_2OFe$ C, 47 56, H, 3 00, N, 13 88%)

Ammonium dicyanocyclopentadienylcarbonylferrate (II) Addition of excess ether to a filtered, ammonia saturated, ethanolic solution of $H[Fe(CN)_2(C_5H_5)(CO)]$ precipitated the ammonium salt as a yellow, microcrystalline powder Recrystallization from ethanol-ether gave yellow crystals soluble in water, alcohol and polar organic solvents but insoluble in ether and benzene This salt is more air-sensitive than the potassium salt, but it is also more convenient to use since it is easier to purify and is much more soluble in organic solvents (Found C, 44 05, H, 4 14, N 19 34, Fe, 25 53 Calcd for $C_8H_9N_3OFe$ C, 43 87, H 4 14, N, 19 19, Fe, 25 48%)

Potassium chlorocyclopentadienyltricarbonyltungstate (II) Following Fischer(12), a mixture of lithium cyclopentadienide (0 11 mole) and tungsten hexacarbonyl (0 10 mole) in 300 ml of dimethylformamide (dried by passing over Linde Molecular Sieve" 5A) was slowly heated to 100 and held there for 2 hr To the resulting cooled solution of $Li[W(C_5H_5)(CO)_3]$, under nitrogen, there was added 300 ml of water 500 ml of ether and 7 ml of acetic acid, precipitating light yellow air sensitive $H[W(C_5H_5)(CO)_3]$ Addition of 30 ml of carbon tetrachloride to the stirred mixture caused the yellow precipitate to disappear within 5 min and the red colour which developed was extracted largely into the ether phase The phases were separated and the water layer washed twice with 100 ml portions of ether and then the combined ether phases were dried over sodium sulphate Evaporation of solvent gave a brown residue which was taken up in 150 ml of acetone and stirred with activated charcoal for 0 5 hr at room temperature Addition of water to the filtered solution until a solid appeared on the surface followed by cooling overnight at 0 gave deep red crystals m p 160 (dec) A second crop of crystals from the mother liquor gave a total yield to 28 8 g (78 per cent) (Found C, 26 07 H, 1 38 Calcd for $C_8H_5O_3ClW$ C 26 08, H, 1 36%)

This procedure which is an adaptation of Fischer's's(12) preparation of $Li[Mo(C_5H_5)(CO)_3]$ and Wilkinson's(13) oxidation of the lithium salt to the chloride, also gave $[MoCl(C_5H_5)(CO)_3]$ in 80 per cent yield Attempts to prepare $[CrCl(C_5H_5)(CO)_3]$ by this method were unsuccessful

Potassium dicyanocyclopentadienyldicarbonylmolybdate (II) A solution of 7 g (0 025 mole) of $[MoCl(C_5H_5)(CO)_3]$ and 3 30 g (0 051 mole) of potassium cyanide in 180 ml of methanol was warmed to reflux and held there (0 5 hr) until no more gas was evolved About one mole of carbon monoxide was evolved per mole of complex The cooled solution was filtered and the residue washed with methanol Evaporation of solvent from the combined filtrates left an oily mixture of white and yellow solids Extraction of this residue with 200 ml of ethanol and evaporation of the solvent gave 6 0 g (80 per cent) of yellow powder after washing with ether and drying *in vacuo* The powder was very hygroscopic and good analytical data were not obtained An infra-red spectrum showed broad metal carbonyl peaks at 1875 cm^{-1} and 1960 cm^{-1} and cyanide peaks at 2060 cm^{-1} and 2090 cm^{-1} in agreement with the proposed structure

Potassium dicyanocyclopentadienyldicarbonyltungstate (II) Application of the preceding procedure to $[WCl(C_5H_5)(CO)_3]$ gave a yellow solid Chromatography of an ethanol solution of the mixture on alumina gave two bands, one eluted by ethanol and the other eluted by water The ethanol band contained the monocyanide described below Evaporation of solvent from the water band gave a yellow residue which was taken up in ethanol The solution was filtered and then evaporated to a yellow powder which was washed with methylene chloride and dried *in vacuo* This material was also very hygroscopic An infra-red spectrum showed metal carbonyl bands at 1860 and 1950 cm^{-1} and an incompletely resolved cyanide doublet at 2085, 2100 cm^{-1} Except for the smaller splitting of the cyanide bands, the spectrum (from 2 5 to 15 μ) was very similar to that of the analogous molybdenum complex

Cyanocyclopentadienyltricarbonyltungsten (II) A stirred solution of 37 g (0 10 mole) of $[WCl(C_5H_5)(CO)_3]$ in 200 ml of ethanol was brought to reflux in a flask shielded from light and then a solution of 7 g (0 11 mole) of potassium cyanide in 25 ml of water was added dropwise during 0 5 hr About 0 016 mole of carbon monoxide was evolved during 1 3 hr at reflux The cooled solution was evaporated to near dryness and extracted with chloroform Chromatographing this solution on alumina gave a yellow band eluted by ethanol Evaporation of solvent and crystallization of the residue from chloroform–petroleum ether and then from benzene gave orange, light sensitive crystals, m.p. 201.5–202°. An infra-red spectrum showed metal carbonyl bands at 1970 cm^{-1} (*vs*) and 2060 cm^{-1} (*s*) and a cyanide band at 2120 cm^{-1} (*m*). The complex was a non-electrolyte in nitrobenzene. (Found: C, 30.18; H, 1.40; N, 4.11; W, 51.10; mol. wt., 377 in benzene. Calcd. for $C_9H_5NO_3W$: C, 30.11; H, 1.40; N, 3.90; W, 51.23%; mol. wt., 359.)

---

(12) E O Fischer, W Hafner and H O Stahl, *Z Anorg Chem* **287**, 47 (1955)

(13) T S Piper and G Wilkinson, *Naturwisserchaften* **42**, 625 (1955)

Cyclopentadienylcarbonyl-bis-(methyl isocyanide)iron (II) *iodide.* A mixture of 4.8 g (0.020 mole) of $K[Fe(CN)_2(C_5H_5)(CO)]$ and 30 ml of methyl iodide in 150 ml of acetonitrile was refluxed for 20 hr. The resulting solution was filtered and evaporated to dryness under reduced pressure. After taking the residue up in methylene chloride, the solution was filtered and excess petroleum ether was added to precipitate 5.4 g (75 per cent yield) of yellow powder. Recrystallization from chloroform–hexane gave small yellow crystals, m.p. 220–1° (dec.), soluble in water and all but least polar organic solvents. The complex had a molar conductance of 91 in water (23°, 1.00 × 10^{-3} molar) but the odour of isocyanide over the solution showed that some decomposition had occurred. In nitrobenzene the molar conductance was 28.1 (23°, 1.99 × 10^{-3} molar). (Found: C, 33.25; H, 3.16; N, 8.11. Calcd. for $C_{10}H_{11}N_2OIFe$: C, 33.45; H, 3.09; N, 7.81%.)

Cyclopentadienylcarbonyl-bis-(allyl isocyanide)iron (II) *bromide.* A mixture of 7.2 g (0.030 mole) of $K[Fe(CN)_2(C_5H_5)(CO)]$ and 8.5 ml (about 0.1 mole) of allyl bromide in 175 ml of acetonitrile was refluxed for 18 hr. The solution was filtered and evaporated to dryness and the residual thick oil was taken up in acetonitrile. This solution was filtered, excess ether was added and the solution was allowed to stand about 4 hr until the oil crystallized. Recrystallization from acetonitrile–ether gave a 35 per cent yield of yellow-brown crystals, m.p. 110–13°, with a powerful isocyanide odour. (Found: C, 46.38; H, 4.26; N, 7.62. Calcd. for $C_{11}H_{1}N_2OBrFe$: C, 46.31; H, 4.16; N, 7.71%.)

Cyclopentadienylcarbonyl-bis-(benzyl isocyanide)iron (II) *bromide.* A mixture of 80 g (0.33 mole) of $K[Fe(CN)_2(C_5H_5)(CO)]$ and 100 ml (about 20 per cent excess) of benzyl bromide in 300 ml of acetonitrile was refluxed for 12 hr and then cooled, filtered and evaporated to dryness. Crystallization from acetonitrile–ether gave an oil which crystallized on standing. Recrystallization from the same solvent gave 112 g (72 per cent yield) of golden-yellow crystals, m.p. 132.5–133.5°, soluble in polar solvents. The complex had molar conductances of 89.7 (0.995 × 10^{-3} molar), 122 (0.199 × 10^{-3} molar) and 121 (0.398 × 10^{-4} molar) in water at 23°. In nitrobenzene the conductance was 24.6 (23°, 0.199 × 10^{-3} molar). (Found: C, 57.05; H, 4.10; N, 5.91; Fe, 12.0. Calcd. for $C_{22}H_{19}N_2OBrFe$: C, 57.06; H, 4.14; N, 6.06; Fe, 12.1%.)

Cyanocyclopentadienylcarbonyl(p-carbethoxybenzyl isocyanide)iron (II). A mixture of 2.4 g (0.010 mole) of $K[Fe(CN)_2(C_5H_5)(CO)]$ and 2.45 g (0.010 mole) of *p*-carbethoxybenzyl bromide in 100 ml of acetonitrile was refluxed overnight and then the solvent was evaporated at reduced pressure. Addition of petroleum ether to a methylene chloride solution of the residue precipitated oily yellow crystals which were recrystallized from methanol–water as a mustard-yellow powder (50 per cent yield), m.p. 166–166.5°. The complex showed the expected phenyl and carboxylic ester peaks in the infra-red and was soluble in most organic solvents. (Found: C, 59.49; H, 4.63; N, 7.42. Calcd. for $C_{18}H_{16}N_2O_3Fe$: C, 59.36; H, 4.43; N, 7.69%.)

Cyanocyclopentadienylcarbonyl(p-carboxybenzyl isocyanide)iron (II). Hydrolysis of the ester group in the preceding complex was accomplished by heating at 100° in 0.4 molar hydrochloric acid for 6 hr. After this treatment, two-thirds of the complex had dissolved. Isolation of the acid and recrystallization from ethanol–water gave a 52 per cent yield of yellow crystals, m.p. 167.5–168.5°. An infra-red spectrum showed a carboxylic acid. (Found: C, 56.52; H, 4.04; N, 7.76; Fe, 16.70. Calcd. for $C_{16}H_{12}N_2O_3Fe$: C, 57.17; H, 3.60; N, 8.34; Fe, 16.62%.)

Cyanocyclopentadienylcarbonyl(p-chlorobenzyl isocyanide)iron (II). Reaction of equimolar quantities of $K[Fe(CN)_2(C_5H_5)(CO)]$ and *p*-chlorobenzyl bromide in acetonitrile for 16 hr followed by the usual work-up gave yellow crystals contaminated with a tarry impurity. Purification by chromatography of a benzene solution of the product on alumina and recrystallization of the major component gave yellow crystals, m.p. 113–15°. (Found: C, 55.10; H, 3.58; N, 8.60; Fe, 16.92. Calcd. for $C_{15}H_{11}N_2OClFe$: C, 55.16; H, 3.40; N, 8.58; Fe, 17.10%.)

Cyanocyclopentadienylcarbonyl(triphenylmethyl isocyanide)iron (II). A mixture of 2.4 g (0.010 mole) of $K[Fe(CN)_2(C_5H_5)(CO)]$ and 3.3 g (0.010 mole) of triphenylmethyl bromide in 75 ml of acetonitrile was refluxed for 16 hr. Evaporation of solvent left a glass which was extracted with methylene chloride and precipitated with petroleum ether. Recrystallization from methyl ethyl ketone–petroleum ether gave a 50 per cent yield of yellow brown crystals, m.p. 181–3° (dec.). (Found: C, 73.33; H, 4.79; N, 6.11. Calcd. for $C_{27}H_{20}N_2OFe$: C, 72.98; H, 4.54; N, 6.31%.)

Cyanocyclopentadienylcarbonyl(benzyl isocyanide)iron (II). This complex was obtained as a brown oil by the reaction of equimolar quantities of $K[Fe(CN)_2(C_5H_5)(CO)]$ and benzyl bromide in acetonitrile followed by the usual work-up. The identity of this and the following complex rests on the infra-red spectra (see Table 1 for the 2000 cm^{-1} region) since they could not be purified by recrystallization or distillation.

Cyanocyclopentadienylcarbonyl(allyl isocyanide)iron (II). This complex was obtained as a viscous brown oil from the reaction of equimolar quantities of allyl bromide and $K[Fe(CN)_2(C_5H_5)(CO)]$ followed by the usual work-up.

Cyclopentadienylcarbonyl-bis-(methyl isocyanide)molybdenum (II) *iodide*. A mixture of 3.1 g (0.01 mole) of $K[Mo(CN)_2(C_5H_5)(CO)_2]$ and 10 ml of methyl iodide in 100 ml of acetonitrile was refluxed overnight. The resulting solution was evaporated to dryness and the residue was extracted with hot methylene chloride. Addition of petroleum ether precipitated a yellow powder which was reprecipitated from acetonitrile by addition of ether to produce a mustard yellow, microcrystalline powder, m.p. 180–2°. An infra-red spectrum showed metal carbonyl bands at 1945 and 2000 cm^{-1} and an incompletely resolved isocyanide doublet at 2185, 2200 cm^{-1}. (Found: C, 30.94; H, 2.80; N, 6.57. Calcd. for $C_{11}H_{11}N_2O_2IMo$: C, 31.00; H, 2.61; N, 6.57%.)

Attempts to alkylate $K[W(CN)_2(C_5H_5)(CO)_2]$ by this procedure gave only small yields of the monoisocyanide complex described below.

Cyclopentadienyltricarbonyl(methyl isocyanide)tungsten (II) *iodide*. A solution of 5 g of $[W(CN)(C_5H_5)(CO)_3]$ and 50 ml of methyl iodide in 100 ml of acetonitrile was refluxed for 14 hr in darkness. The cloudy solution was then filtered and evaporated to 5.2 g of residue which was taken up in chloroform and chromatographed on alumina. Ethanol eluted a band containing 4.25 g of starting complex. A second band remained on the column and was removed manually. Extraction of the second band with acetonitrile and precipitation with ether gave 0.41 g of light sensitive, yellow powder which melted at 153.0–153.2° with gas evolution, resolidified at 158° and remelted at 191–5° (dec.). The yield, based on 0.75 g (0.0021 mole) of starting material, was 39 per cent. An infra-red spectrum showed metal carbonyl bands at 1985 cm^{-1} (*vs*) and 2080 cm^{-1} (*s*) and an isocyanide band at 2230 cm^{-1} (*m*). (Found: C, 23.76; H, 1.72; N, 3.24; W, 36.42. Calcd. for $C_{10}H_8NO_3IW$: C, 23.97; H, 1.61; N, 2.80; W, 36.70%.)

Acknowledgements. The author is grateful to Dr. H. M. HUBBARD for reviewing the manuscript and to Dr. F. A. C. ALLISON and Dr. W. Z. HELDT for valuable discussions.

[illegible] Chem 1963 Vol 25, pp 187 to 194 Pergamon Press Ltd Printed in Northern Ireland

THE REACTION BETWEEN METALLIC POTASSIUM AND CARBON MONOXIDE. THE PRECURSORS OF THE POTASSIUM SALT OF HEXAHYDROXYBENZENE

W. F. SAGER, A FATIADI, P C PARKS, D G WHITE and T P PERROS
Department of Chemistry, The George Washington University, Washington, D C

(*Received* 27 *June* 1962)

Abstract—Thermal measurements and magnetic susceptibility determinations have been made on the highly reactive materials, with various overall compositions, that result when increasing amounts of carbon monoxide are allowed to react with metallic potassium These studies indicate consecutive formation of two diamagnetic solid products of empirical formulae $K_3C_2O_2$ and KCO which form prior to the reported final product, $K_6C_6O_6$, the potassium salt of hexahydroxybenzene Methylation of the compound KCO with methyl iodide leads to a product $C_4O_4(Me)_4$, resulting from the uptake of four methyl groups, two bound to carbon and two to oxygen These results are indicative of a structure (O C C C C O)$^{4-}$, 4K$^+$ for the intermediate KCO

O O

MANY *of the active metals of Groups I and II are known to react with carbon monoxide when dissolved in liquid ammonia* Thus the reaction of potassium in liquid ammonia yields a very reactive carbonyl with the composition KCO, and this solid substance, when freshly prepared, has been described as pale red in colour and to decompose explosively when heated to about 100°C [1] JOANNIS[2] suggested the formulation $K_2C_2O_2$ for this substance, since when he treated it with water and acidified the resulting alkaline mixture, glycolic acid was isolated Accordingly, the following reaction with water was proposed

$$K_2C_2O_2 + 2H_2O \rightarrow HOCH_2CO_2K + KOH \tag{1}$$

Other carbonyls of the active metals prepared in a similar fashion include those of sodium[1] barium,[3] strontium,[4] and lithium, rubidium and calcium[5] All these polar compounds are reported to undergo thermal decomposition to yield carbon plus the metal oxide and carbonate, and no evidence for the formation of salts of organic substances was obtained

In unique contrast to the above information, potassium is the only alkali metal which has been reported to combine directly in the solid state with carbon monoxide Furthermore, the course of this reaction appears to be different from that occurring in liquid ammonia solution, since the end product is a relatively stable gray solid On acidification of this solid, hexahydroxybenzene was isolated, and for this reason the reaction product was identified as the potassium salt of hexahydroxybenzene, $K_6C_6O_6$ [6]

Early observers[6,7] of the behaviour of metallic potassium with carbon monoxide noted that the exothermic process involved several stages Although only the final stage was subjected to chemical investigation the changes in appearance do give some inkling of the steps through which the final product is achieved It was observed that the originally dull potassium surface acquired a brilliant silver lustre after an interval of exposure to the gas After a period of time the product became gray, then deep black and the rate of absorption increased as the reaction neared completion It was also noted that when most of the material had become black, a rapid and very exothermic reaction took place in which the black mass was converted to the gray $K_6C_6O_6$

---

[1] A JOANNIS, *C R Acad Sci, Paris* **116,** 1518 (1893)
[2] A JOANNIS *C R Acad Sci, Paris* **158,** 874 (1914)
[3] GUNTZ and MENTREL, *Bull Soc Chim France* **29,** 585 (1903)
[4] G ROEDERER, *Bull Soc Chim France* **35,** 715 (1906)
[5] T G PEARSON *Nature Lond* **131,** 166 (1933)
[6] R NIETZKI and T BENCKISER *Ber Dtsch Chem Ges* **18,** 1834 (1885)
[7] J LIEBIG *Ann* **11,** 182 (1834) B BRODIE, *Ann* **113,** 358 (1860)

More recently, SHUSHUNOV[8] has investigated the kinetics of the reaction of carbon monoxide with a thin film of potassium metal condensed in a vacuum on a copper foil Although induction periods were noted, absorption of carbon monoxide occurred even at temperatures as low as 183 C Under these conditions $K_6C_6O_6$ was said to be the product at temperatures above 170 K, but a pyrophoric solid resulted at lower temperatures On the basis of the fact that the latter compound absorbed a total of one mole of water vapour per formula weight of KCO, which is in accordance with Equation (1), SHUSHUNOV has suggested the IOANNIS formula $K_2C_2O_2$ for this substance[9]

Our initial study of the reaction of carbon monoxide with gramme quantities of metallic potassium at ordinary temperatures allowed us to make the following additional observations If the potassium surface is clean no induction period is apparent A considerable amount of carbon monoxide about ten mole per cent, is absorbed before the surface of the material loses its silvery lustre and malleability There is, however, extensive shrinkage during this stage In agreement with previous observations,[8] the rate of absorption is much greater when the temperature is below the melting point of the metal If the rate of carbon monoxide addition is restricted toward the end of the reaction so that the mixture does not become too hot, the final change from black to gray does not occur and hexahydroxybenzene cannot be isolated on acidification of the black pyrophoric product

The investigations to be described were undertaken to gain some insight into the various stages of this reaction and, in particular, to determine the nature of the material with the silvery appearance which is formed at the outset

EXPERIMENTAL

Materials Carbon monoxide was generated by the dropwise addition of formic acid (Eastman Chemical, practical grade 90 per cent) to a large excess of concentrated H_2SO_4 The product was purified by passage through concentrated H_2SO_4 ascarite and P_2O_5 traps Prior to collection the train was purged by allowing the generator to operate slowly overnight, and the formic acid was freed of dissolved air by allowing some CO to pass upward through the dropping funnel Both ends of the generating train were protected from the atmosphere by mercury seals The gas was collected and stored in flasks on a vacuum line which had been evacuated to about 10^{-3} mm prior to filling

Potassium metal (Fisher Chemical) was vacuum-distilled with exclusion of mercury vapour into glass ampoules The melting point of a representative sample (see Table 1) was 63 45 C The literature value is 63 7 , the presence of only about 0 1 per cent sodium in our samples could account for the difference[10]

Thermal measurements The equipment shown in Fig 1 was designed in order to determine the solubility, if any, of the K CO reaction product in excess potassium by measuring its effect on the melting point and fusion process of the metal. A weighed amount of potassium (*I* in Fig. 1) was introduced under high vacuum from an ampoule (then removed) into its Dewar-like cell (*H*), which was attached to the vacuum line at (*A*). Reaction materials of known overall composition were prepared directly in the cell by admitting, through line (*E*), measured increments of CO gas. After each addition, a homogeneous material was obtained by melting and stirring it with the magnetic stirrer (*J*) for about 15 min. The silvered jacket of the cell could be evacuated to the desired vacuum through line (*D*). The cell, its accessories, a thermometer (*B*) with 0.1° divisions, and a high-speed stirrer (*C*) to insure thermal homogeneity were surrounded by a shield of aluminum foil (*L*) and placed in a large Dewar jug (*M*) fitted with an insulated cover (*F*). The contents of the cell were heated at a small and constant rate by means of the tiny internal filament (*N*) powered by a parallel pack of batteries. Any temperature difference existing between that registered by the thermometer and that in the reaction cell could be measured by the three-junction thermopile (*G*). In order to compensate for any heat loss from the apparatus, an external heater (*K*) in the Dewar jug was manually regulated so as to maintain this temperature difference within a few hundredths of a degree.

---

[8] V A SHUSHUNOV, *Zh Fiz Khim* **23,** 1322 (1949), *Chem Abstr* **44,** 2833 (1950), M B NEIMAN and V A SHUSHUNOV, *Dokl Akad Nauk SSSR* **60,** 1347 (1950), *Chem Abstr* **45,** 425 (1951)

[9] V A SHUSHUNOV, *Trudy Komissii Anal Khim Akad Nauk SSSR* **3,** 146 (1951), *Chem Abstr* **47,** 2623 (1953)

[10] S L WALTERS and R R MILLER, *Analyt Chem* **18,** 468 (1946)

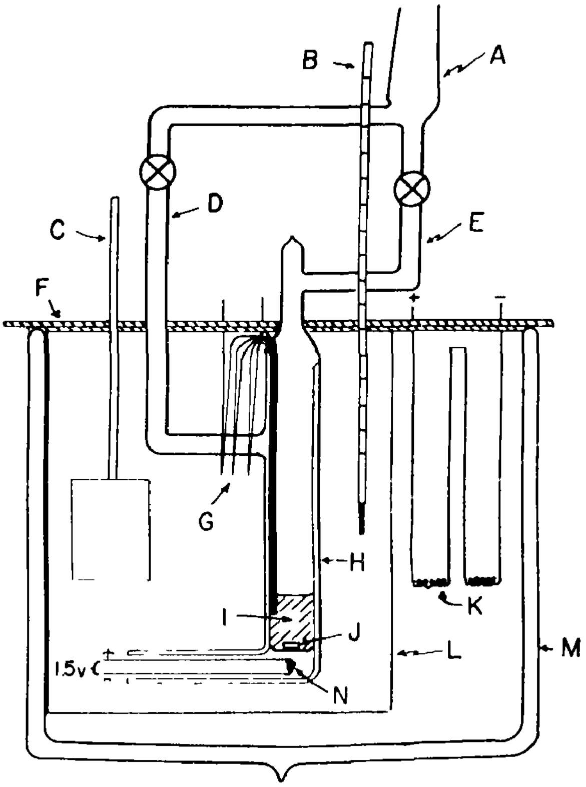


Fig. 1. Apparatus for thermal measurements.

Fig. 2 represents a typical time-temperature relationship obtained by this procedure; this particular curve was that observed with a K/CO mole ratio of 6.50. At this and at other compositions where some fusion did occur, the melting point did not vary significantly from that of the original sample of potassium. Actually, because of slight temperature variations in the surrounding air bath the melting points obtained from these curves were not sufficiently precise. Therefore separate measurements of the melting points were made from cooling curves obtained while the air bath was vigorously stirred.

Since the rate of heat input was constant throughout all these determinations, the time required to melt the unreacted potassium in the product mixture (and measured from the length of the vertical line as illustrated in Fig. 2) was proportional to the heat absorbed by this fusion process. The proportionality constant was determined from the melting curve for the sample of pure potassium and the value for the heat of fusion of this metal, 14.6 cal/g(1) or 571 cal/mole.

---

(1) E. Rengade, *C.R. Acad. Sci. Paris* **156**, 1897 (1913).

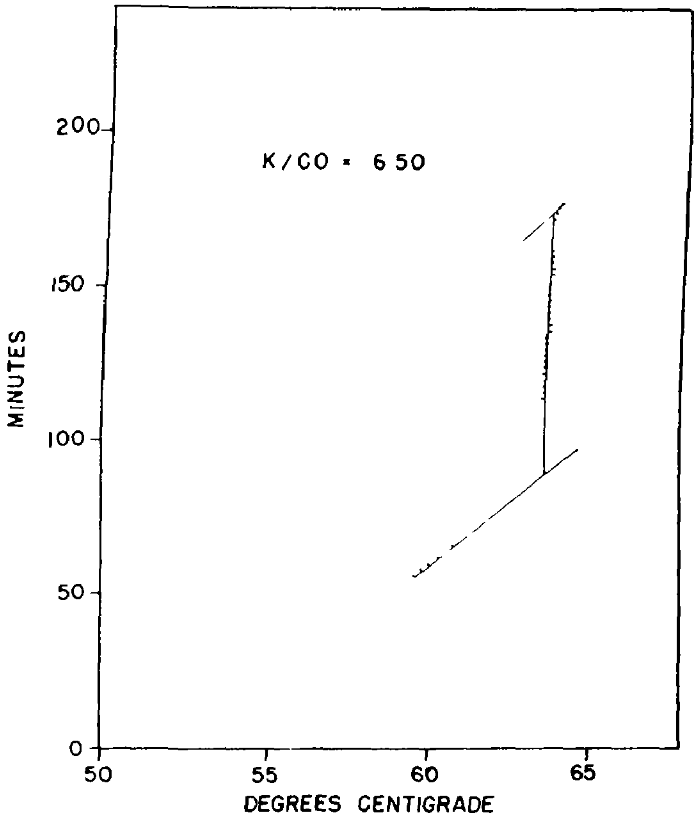


FIG. 2.—Heating curve of a reaction mixture with an overall composition corresponding to a mole ratio of K/CO = 6.50.

TABLE I.—THERMAL MEASUREMENTS OF POTASSIUM CARBON MONOXIDE REACTION MIXTURES

Weight of K Sample (g)	CO/K Mole Ratio	m.p. (°C)	Cal (per mole of total K) required to melt unreacted K
4.1374	0	*	571
	0.0199	*	561
	0.0549	*	530
	0.0898	63.23	498
	0.125	63.42	477
	0.160	63.45	364
	0.196	63.45	392
	0.254	63.53	336
	0.337	63.54	295
	0.659	None	0
4.1417	0	63.45	571
	0.0077	63.55	547
	0.0161	63.43	522
	0.0513	63.44	*
	0.154	63.57	425
	0.334	63.64	240
	0.413	63.67	212
	0.527	†	40†
	1.007	None	0

* Not determined † Uncertain

Table 1 records the melting points of the unreacted potassium at various overall CO/K compositions together with the calories required to melt this potassium per mole of total potassium (combined and uncombined). Determinations employing two different original samples of the metal are tabulated.

It will be noted that the measurements obtained at a CO/K ratio of 0.527 are uncertain, since so little unreacted potassium remained at this point, the heated product was too stiff to stir, and homogeneity of the mixture could not be maintained. The final CO/K ratio of 1.007, which is in good agreement with the formula KCO, was the value obtained when combination of CO with the product, which was entirely black at this stage, was complete.

Magnetic determinations. Magnetic susceptibility values at room temperature were determined on a quartz helix balance patterned after that described by SENFTLE.[(12)] Several samples of various carbon monoxide-potassium product mixtures were prepared in thin-walled glass bulbs, of about 3 mm diameter, which were then evacuated and sealed. After each magnetic measurement, the bulb was broken, its contents analysed, and a correction was applied for the susceptibility of the glass. The apparatus was calibrated using a bulb containing potassium alone, and our results given below are based on the reported[(13)] atomic susceptibility of 21.5×10^{-6} (or 0.550×10^{-6} per g) for this metal at 20°C.

Two different product mixtures with approximate overall compositions corresponding to CO/K mole ratios of 0.24 and 0.37, and both containing visible amounts of excess potassium, had gram susceptibilities of 0.30 and 0.092 ($\times 10^{-6}$), respectively. A sample of the black product, KCO, prepared in the presence of excess CO, was diamagnetic with a value of -0.086×10^{-6} g^{-1}.

X-ray powder pattern of KCO. A Debye-Scherrer diffraction pattern of the black product with the empirical formula KCO was obtained using a camera of 114.6 mm diameter and CuK_α radiation. Interplanar spacings and relative intensities of the lines are given in Table 2.

TABLE 2.—X-RAY DIFFRACTION PATTERN OF KCO

d (Å)	Intensity*	*d* (Å)	Intensity*
3.18	*s*	1.62	*vw*
2.88	*m*	1.45	*vw*
2.78	*vs*	1.39	*w*
2.11	*m*(*br*)	1.28	*w*
1.96	*s*	1.24	*w*
1.68	*w*(*br*)	1.16	*w*

*s — strong, *m* — medium, *w* — weak, *v* — very, *br* — broad

Methylation studies. Several procedures were employed for the methylation of the compound KCO.

Reaction without solvent. Approximately 5 g of freshly distilled potassium in a sealed ampoule fitted with a small magnet was introduced into a 500 ml round-bottom flask evacuated to 10^{-3} mm. The ampoule was heated to melt the potassium, then lifted with a magnet and dropped to break the tip. The empty ampoule was then removed and sealed off from the rest of the apparatus. Carbon monoxide was admitted slowly at such a rate that the temperature did not exceed about 80°C. After the reaction was practically complete, the pressure of CO was increased to about 0.5 atm for a period of time. Fifty ml of methyl iodide (Eastman Chemical, white label) was then introduced without exposure of the black reaction product to air. Methylation was extremely slow under these conditions. After one week the yellow-gray solid that had formed was crushed with a rod, and the mixture was allowed to stand for several more hours. The excess CH_3I was evaporated, and the remaining residue was distilled at about 11 mm pressure. The crude distillate, about 3 ml, was redistilled at atmospheric pressure to yield about 2 g of yellow liquid boiling at 220–5°C. This was distilled again, and a middle fraction, b.p. 224.5°, collected.

Methylation in the presence of solvent. A sample of the KCO product was prepared as described above. A solution of 30 ml CH_3I in 70 ml of purified ethylene glycol dimethyl ether was added, and the reaction mixture was stirred magnetically for two days in the absence of air. The excess CH_3I and solvent were removed, and the product was distilled at reduced pressure. Redistillation as before yielded 2.1 g of product. Its infra-red spectrum (see below) was the same as that of the sample prepared without solvent.

Reaction of CO *with* K *in* $CH_3OCH_2CH_2OCH_3$. Carbon monoxide was passed over the liquid surface of ethylene glycol dimethyl ether (purified by distillation in dry nitrogen after treatment with

---

(12) F. E. SENFTLE, M. D. LEE, A. A. MONKEWICZ, J. W. MAYO and T. PANKEY, *Rev. Sci. Instrum.* **29**, 429 (1958).

(13) B. BOHM and W. KLEMM, *Z. Anorg. Chem.* **243**, 69 (1939).

$LiAlH_4$ and K) at 72–75° in which about 5 g of distilled potassium was suspended (very slightly dissolved[14]) with stirring. A gray-yellow crystalline product slowly formed. After one week dry CH_3I was added in excess to methylate the mixture. The solid product (96% KI) was filtered, and upon removal of the solvent from the solution about 2.5 ml of a liquid boiling at 224–5°C was obtained. This was fractionated and the middle fraction of the somewhat impure product was collected for analysis. (Found: C, 56.56; H, 7.45; OCH$_3$, 36.25; molecular weight 165, 158, 188, 191. Calcd. for $C_8H_{12}O_4$: C, 55.80; H, 7.03; 2(OCH$_3$) per molecule 36.04%; molecular weight 172.) Its infra-red spectrum showed absorption peaks at 5.7, 5.9 and 6.1 μ. No 2,4-dinitro-phenylhydrazone derivative could be prepared and an olefinic test with Br_2 in CCl_4 was very weak. Catalytic hydrogenation at 760 mm and 25° was incomplete; a 400 mg sample absorbed only about 13 ml of hydrogen. The odour of the compound was changed however and an infra-red analysis indicated both hydroxyl and carbonyl absorption.

Methylation of a potassium-rich intermediate. A mixture of approximate overall composition CO/K = 0.5 was made by the general procedure (without solvent) described above. No appreciable reaction was observed when the mixture was stirred with CH_3I for three days in the absence of a solvent. However, after the addition of purified ethylene glycol dimethyl ether, methylation started immediately. The yellow solid precipitate was filtered and found to contain about 60% KI and a considerable amount of an unknown carbonyl compound. This solid was steam-distilled and acetaldehyde was obtained as a hydrolysis product. The excess CH_3I and solvent were removed from the original filtrate leaving a viscous product boiling at 222–4°C and having an infra-red spectrum identical to that of the high-boiling product obtained by the other procedures.

Polarographic reduction of the methylation product $C_8H_{12}O_4$. Polarograms were recorded for saturated solutions of this slightly-soluble compound in 0.2 M aqueous phosphate buffers at room temperature. A Leeds and Northrup "Polarotron" dropping mercury electrode assembly, a saturated calomel electrode (s.c.e.) and a L & N Electro-Chemograph (Type E) instrument were employed. Methyl cellulose was used as a maximum suppressor. In the interpretation of the curves, the current was arbitrarily chosen to be the maximum current per drop and a correction for residual current, measured in a 0.2 M solution of pH 10.7 buffer, was applied.

TABLE 3. POLAROGRAPHIC REDUCTION OF SATURATED AQUEOUS BUFFERED SOLUTIONS OF $C_8H_{12}O_4$

	pH	$E_{1/2}$(v vs s.c.e.)	i_d(μamp)	No. of electrons involved*
First	9.7	1.040	111	0.99
wave	10.7	1.040	202	1.16
Second	9.7	1.425	98	0.89
wave	10.7	1.371	123	1.57

* Calculated from the slopes of the linear plots of $E_{d.e.}$ vs log $i/(i_d - i)$, assuming reversible electrode reactions.

Table 3 summarizes the data for the two reduction waves that were observed under alkaline conditions, i.e. at pH 9.7 and 10.7. Although the first reduction wave corresponded to a single electron transfer, the second wave was almost certainly not a simple reduction to a dihydro derivative. Its pH dependence and the fractional values for the number of electrons transferred suggest that the second wave was a catalytic hydrogen evolution wave of the kind reported by RYVOLOVA[15] for dibenzoylethylene and other unsaturated 1,4-diketones.

DISCUSSION

Melting-point determinations (Table 1) indicate that the solid product which is first formed when a limited amount of carbon monoxide reacts with potassium is insoluble in the excess metal. The melting point of the remaining potassium was not depressed but did in fact increase by 0.2–0.3°, which was presumably the result of an interaction that consumed a trace amount of a metal-soluble impurity present in the original samples of potassium.

[14] J. L. DOWN, J. LEWIS, B. MOORE and G. WILKINSON, *J. Chem. Soc.* 3767 (1959).

[15] A. RYVOLOVA, *Collection Czechoslov. Chem. Commun.* **22,** 1114 (1957).

Since the surface of the reaction mixture retains its silvery appearance even after a considerable amount of carbon monoxide has been absorbed, it is concluded that the metal-insoluble reaction product is readily wetted and obscured by the uncombined potassium. In agreement with this conclusion is the following observation. When zones of a black product eventually do become visible, these quickly vanish and the material regains its silvery lustre if the temperature is allowed to rise above the melting point of potassium, either by external warming or simply as a result of the exothermic nature of the reaction.

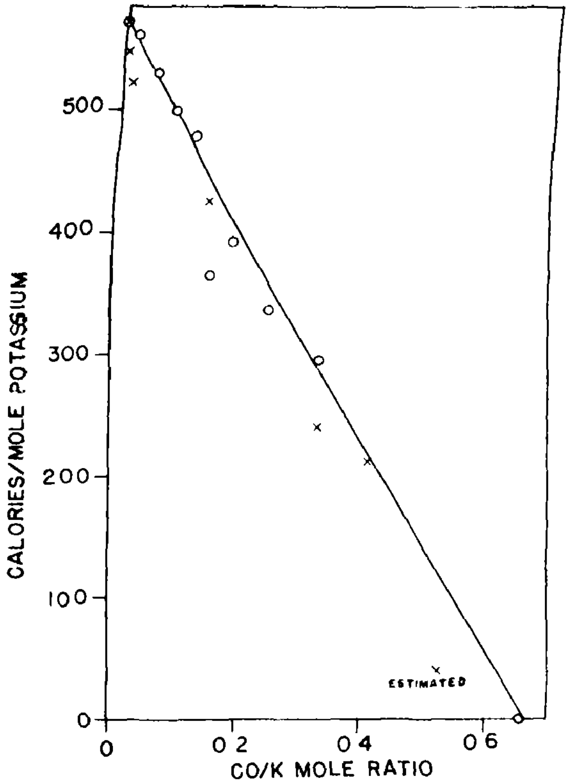


FIG. 3.—Calories (per mole of total K) required to melt the unreacted potassium in various reaction mixtures vs. the CO/K mole ratio.

The formula of this first product of the reaction may be determined by an examination of Fig. 3 which shows the relationship between the quantity of heat required to melt the uncombined potassium and the overall composition of the reaction mixture. The plot is essentially linear as would be expected if a product of fixed composition is formed. The deviations from the straight-line relationship, particularly that at a CO/K mole ratio of 0.527, are attributed to a lack of uniformity in the reaction mixtures. The intercept on the composition axis corresponds to the point at which the last bit of free potassium disappears. Since the value of the CO/K mole ratio at this intercept is about 0.66, this indicates that this first product has the empirical formula $K_3C_2O_2$.

The product with the composition $K_3C_2O_2$ is black and appears homogeneous. However, this solid still retains a high affinity for carbon monoxide, and it reacts readily with additional gas until another product, also black in colour, is obtained with the empirical formula KCO As noted earlier this second compound at a moderate temperature (ca 100–200°) can undergo a rapid and very exothermic rearrangement to yield the gray solid, $K_6C_6O_6$

The above information indicates that the reaction of carbon monoxide with metallic potassium proceeds through the following three stages

$$K + CO \longrightarrow (K_3C_2O_2)_x + CO \longrightarrow (KCO)_x \xrightarrow{\text{heat}} K_6C_6O_6$$

There is no visible evidence for the presence of two solid phases during the second stage of the reaction and it is conceivable that those product mixtures which have compositions intermediate between that of $K_3C_2O_2$ and KCO are solid solutions The two solids with these formulas are both pyrophoric and very similar in appearance, although it was noted that the latter compound can be pulverized much nore easily (in an inert atmosphere)

Magnetic susceptibility measurements show that these products of the potassium-carbon monoxide reaction are diamagnetic This finding is at variance with the measurements reported by ASMUSSEN(16) However, he was working with a product prepared by the reaction of potassium with a mixture of carbon monoxide and carbon dioxide and no doubt was dealing with a different material

The reaction of the crystalline substance (KCO)$_x$ with methyl iodide yields a high boiling liquid, $C_8H_{12}O_4$, as the principal product The methylation is accelerated in the presence of ethylene glycol dimethyl ether An analysis of the product proves the existence of two methoxy groups in the molecule This is consonant with either of the following structural formulae $CH_3COC(OCH_3){=}C(OCH_3)COCH_3$ or CH_3COCO $C(OCH_3){=}C(OCH_3)CH_3$ *Cis-trans* isomerism can be expected with either formulation We do not have sufficient evidence to assign an exact structure to the methylation product Support for an unsaturated diketone structure is obtained, however, from the fact that polarographic reduction of this compound shows a first reduction wave which, in alkaline solution, corresponds to a single electron transfer Such behaviour, unusual for organic compounds, is in accord with a structure analogous to that of quinones, which are well known to undergo rapid and reversible single electron reductions in alkaline solution to give semiquinone ion radicals

The formation of this methylation product, $C_4O_4(CH_3)_4$, indicates the presence of an acylic $C_4O_4^{4-}$ anion in the black compound KCO This anion would be resonance-stabilized, and a conjecture is that a similarly stabilized anion, $C_4O_4^{6-}$, may be a structural feature of the intermediate product with the empirical formula $K_3C_2O_2$

There is the remaining question of the relationship, if any, between the black compound KCO, i e $K_4C_4O_4$, and the product obtained by JOANNIS(1 2) when carbon monoxide was allowed to react with potassium dissolved in liquid ammonia Discounting the differences in certain reported properties, it is conceivable that the latter material also contains the $C_4O_4^{4-}$ anion The evidence presented by JOANNIS for the formula $K_2C_2O_2$ is not convincing, since it is quite reasonable to expect that the hydrolysis of $C_4O_4^{4-}$ under basic conditions would result in cleavage and also yield the glycolate ion as an ultimate product

Acknowledgement The authors wish to acknowledge the support of this work by the Directorate of Chemical Sciences, Air Force Office of Scientific Research

---

(16) P W SELWOOD, *Magnetochemistry* (2nd Ed) p 265, see ref 132 Interscience, New York (1956)

J Inorg Nucl Chem , 1963, Vol 25 pp 195 to 199 Pergamon Press Ltd Printed in Northern Ireland

ORGANIC SALTS OF LANTHANIDE ELEMENTS—I

PREPARATION OF TRI-ACYLATES OF LANTHANUM AND CERIUM(III) FROM AQUEOUS SOLUTIONS

S N Misra, T N Misra, R C Mehrotra*
Chemical Laboratories, Gorakhpur University, Gorakhpur, India

(*Received* 24 *July* 1962)

Abstract Tri-acylates of lanthanum and cerium (III) are quantitatively precipitated by the reaction of their nitrates or chlorides with excess of sodium soaps (laurate, palmitate, stearate) in aqueous solutions These salts are not hydrolysed by water and are soluble in hot benzene from which pure samples may be crystallized Molecular weight measurements show them to be monomeric in benzene Viscosities of their benzene solutions have been measured and their thermogravimetric behaviour has also been investigated Attempts to prepare mixed chloride or nitrate salts were unsuccessful

As a result of extensive work in these laboratories, aluminium acylates have been synthesized as definite compounds (1–3) These derivatives are, however, extremely susceptible to hydrolysis a fact which resulted in controversy for a number of years regarding even their existence (4–9)

In view of this it was considered of interest to study the acylates of heavier tervalent elements, and lanthanum and cerium (III) were chosen for this purpose It was found that even in aqueous solution lanthanum and cerium (III) tri-acylates can be precipitated by treating the nitrate or chloride with sodium carboxylate solution

$$MX_3 + 3NaCOOR \longrightarrow M(OOCR)_3 + 3NaX$$

Attempts to prepare mixed nitrate or chloride salts by taking the reactants in 1 1 or 1 2 molar ratios failed to give mono- or di-acylates It was found that the tri-acylates were precipitated under these circumstances, leaving unreacted metal chloride or nitrate in solution, these results are readily understood, since the reactions should be ionic in aqueous solution

The above salts dissolve in refluxing benzene to give slightly viscous solutions from which pure tri-acylates separate on cooling, and their molecular weights measured ebullioscopically(10) in benzene show them to be monomeric in this solvent In view of the considerable work which has been reported on the viscosities of aluminium soaps[11,12] in non-aqueous solvents, the viscosities of the above salts have been measured in benzene solutions with the following results

---

* Present address Chemistry Dept , University of Rajasthan, Jaipur, India

(1) K C Pande and R C Mehrotra, *J Inorg Nucl Chem* **4**, 128 (1957)

(2) K C Pande and R C Mehrotra, *J Inorg Nucl Chem* 286 (1956)

(3) A K Rai and R C Mehrotra, *J Ind Chem Soc* , **1**, 1 (1962)

(4) J W McBain and W L McLatchie, *J Amer Chem Soc* **54**, 3266 (1932)

(5) W Ostwald and R Riedel , *Kolloid Z* **69**, 185 (1934)

(6) E Eigenberger, *Fett Seifen*, 49, 505 (1940)

(7) K J Mysels , *J Amer Chem Soc* **70**, 1053 (1948)

(8) V R Gray and A E Alexander, *J Phys Chem* **53**, 23 (1949)

(9) C G McGee, *J Amer Chem Soc* , **71**, 278 (1949)

(10) A K Rai and R C Mehrotra, *J Inorg Nucl Chem* , **21**, 311–314 (1961)

(11) T S McRoberts and J H Schulman, *Proc Roy Soc* , A **200**, 136 (1950)

(12) A E Legar, R L Haines, C E Hubley, Z C Hyde and H Sheffer *Canad J Chem* **35**, 799 (1957)

(1) The relative viscosity of their solutions increases with concentration

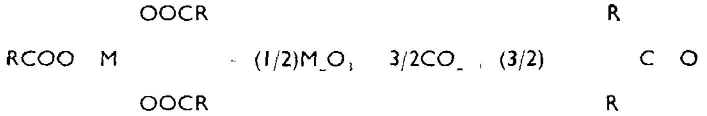
(2) The relative viscosity at the same concentration generally increases with the molecular weight of the parent acid e g

$$\mathrm{M(stearate)_3} \quad \mathrm{M(palmitate)_3} \quad \mathrm{M(laurate)_3}$$

(3) For the same concentration viscosities are in general higher for the cerium (III) salts than for the corresponding lanthanum derivatives

The effect of moisture on the viscometric behaviour of aluminium soaps[11] has been the subject of detailed study In contrast to the tri-acylates, the hydrolysed soaps of aluminium have been shown to exhibit strong gelling tendencies The addition of water to the benzene solutions of lanthanum and cerium (III) salts did not, however, appear to affect their viscosity

Their thermogravimetric behaviour was also investigated with the results shown in Figs 1 and 2 These show that the salts are stable up to ~ 300 C when they begin to decompose slowly according to the following equation



$$\mathrm{RCOO{-}M}\begin{matrix}\mathrm{OOCR}\\ \\ \mathrm{OOCR}\end{matrix} \rightarrow (1/2)\mathrm{M_2O_3} + 3/2\mathrm{CO_2} + (3/2)\begin{matrix}\mathrm{R}\\ \mathrm{C{=}O}\\ \mathrm{R}\end{matrix}$$

Evolution of carbon dioxide appears to be complete at ~ 350–360 °C, after which there is a rapid loss of weight due to decomposition of the ketone Differential weight loss curves give maximum rates of decomposition characteristic of each ketone which are close to those observed in the aluminium acylates To confirm that the ketone is formed initially as a decomposition product a sample of cerium (III) palmitate was heated for about half an hour at 325 C and the palmitone (m p 77–78 °C) was extracted from the heated sample with ethanol The thermogravimetric behaviour of this product was similar to that observed above for the palmitate, with a maximum rate of decomposition at 440 C

The properties of the tri-acylates of lanthanum and cerium (III) show marked differences from the corresponding aluminium compounds Although the latter are also monomeric in benzene, they are highly susceptible to hydrolysis and gel readily The cerium (III) and lanthanum salts appear to be so resistant to hydrolysis that they can be prepared from their aqueous solutions, and the viscosities of their hydrocarbon solutions are unaffected on addition of water These differences result from the more electropositive character of lanthanum and cerium (III)

EXPERIMENTAL

Material

B D H lauric palmitic and stearic acids were further purified by distilling under reduced pressure Benzene was stood over sodium wire, refluxed with metallic sodium and finally dried azeotropically with a small amount of ethanol Lanthanum chloride (Johnson, Matthey, 99 5 per cent pure) was used, cerium (III) nitrate and chloride were B D H laboratory reagent grade

Analytical methods

Metals were estimated as oxides by direct ignition of their organic derivatives Fatty acids were isolated by decomposing the salts with dilute sulphuric acid, the filtered fatty acids were washed thoroughly with cold water to remove traces of mineral acid, dissolved in alcohol, and titrated against standard NaOH solution using phenolphthalein as indicator

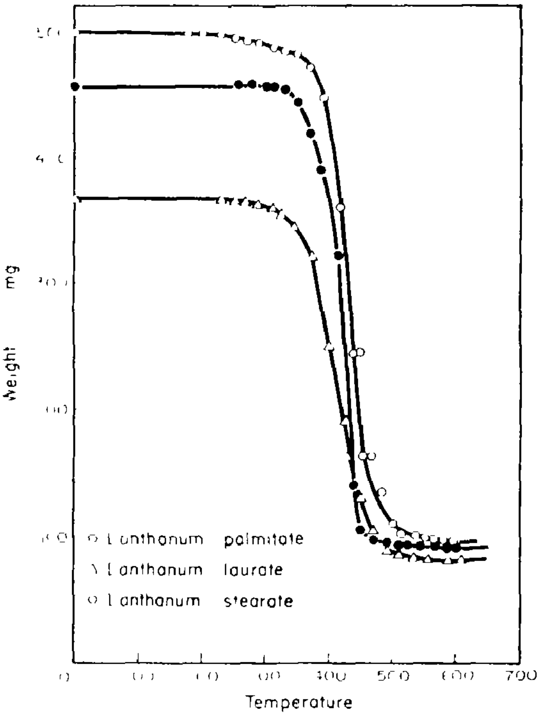

Weight mg
400
300
200
100
0
300
500
600
700
Temperature
Lanthanum palmitate
Lanthanum laurate
Lanthanum stearate

FIG. 1

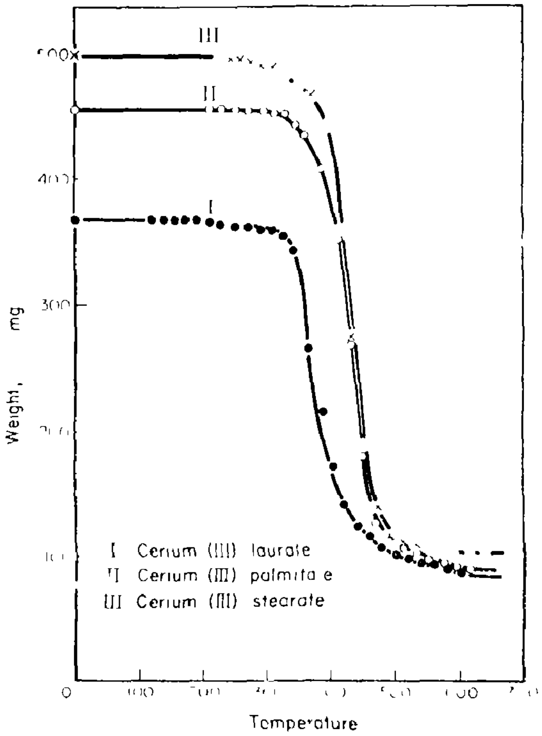

III
II
I
500
400
300
100
Weight, mg
0
100
600
Temperature
I Cerium (III) laurate
II Cerium (III) palmitate
III Cerium (III) stearate

FIG. 2

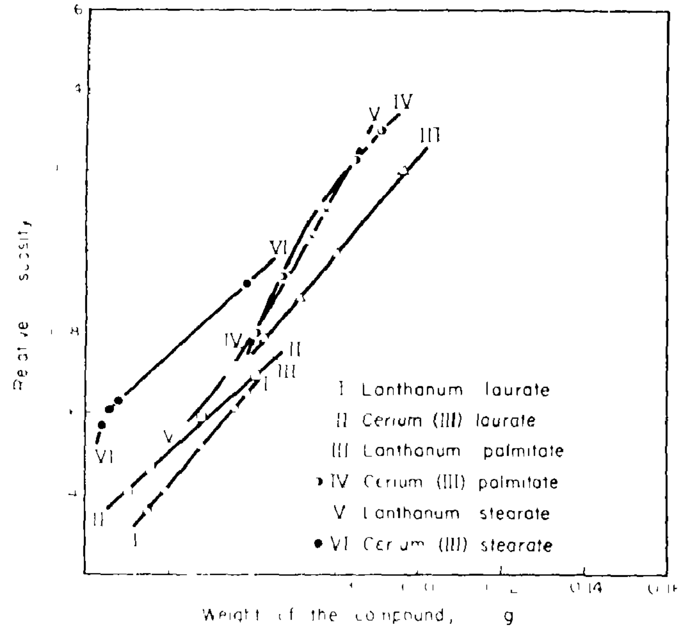


FIG 3

Molecular weights

Molecular weights were determined in benzene with a Gallenkamp semi-micro ebulliometer employing thermistor sensing. Sixteen ml of dry benzene was used, and it was observed that stable observations with benzene as solvent can only be obtained after the addition of some solute. The molecular weight was calculated from the simple relationship $M = KW/R$ where R is the change in resistance of the solvent, M the molecular weight of the solute, W the weight of solute, and K is a constant for the solvent. A linear relationship was observed between W and R, and the molecular weight was calculated graphically from the slope of the line; the average value for K was determined as 77200 with naphthalene as solute.

Preparation of lanthanum tri-laurate

Sodium laurate solution (approximately N/10) was prepared by titrating a known weight of the lauric acid with caustic soda solution using phenolphthalein as indicator. This solution was added dropwise with constant stirring to a cold solution of lanthanum chloride (5.0 g) in water (50.0 g). A

TABLE I — ANALYSIS AND MOLECULAR WEIGHTS OF THE TRI-ACYLATES OF LANTHANUM AND CERIUM (III)

Compound	Analysis				Molecular weight	
	Found		Calculated			
	Metal (%)	Acid (%)	Metal (%)	Acid (%)	Found	Calculated
Lanthanum laurate	18.8	80.8	18.94	81.07	788.0	737.71
Cerium (III) laurate	19.15	80.6	18.99	81.00	786.1	738.1
Lanthanum palmitate	14.91	84.6	15.44	84.56	1000.0	906.05
Cerium (III) palmitate	15.5	86.5	15.48	84.52	1010.0	906.46
Lanthanum stearate	14.14	85.86	14.11	85.89	1079.0	990.17
Cerium (III) stearate	13.91	83.4	14.15	85.85	1085.0	990.62

white precipitate was obtained immediately and the reaction mixture was heated to flocculate the precipitate The precipitate was filtered at room temperature through a Buchner funnel, washed thoroughly with water and then with alcohol to remove traces of sodium laurate

After initial drying in an air oven at 100 105 °C, final drying was carried out under reduced pressure (Yield, 13 9 g, Theoretical yield, 14 0 g Found La, 18 68 Calc for La(OOC $C_{11}H_{23})_3$ La, 18 97 %)

The product was further purified by dissolving in refluxing benzene, on cooling a white amorphous powder crystallized out This was filtered through a sintered funnel (G-4), washed thoroughly with benzene, and finally dried under reduced pressure (Found La, 18 8, $C_{11}H_{23}COO$, 81 03 %)

Analysis and molecular weights for various salts are summarized in Table I

Relative viscosities of tri-acylates of lanthanum and cerium (III)

Viscosities were measured in benzene using a calibrated viscometer at 33 C, and relative viscosities are plotted in Fig 3

Acknowledgement—Two of the authors (S N M , T N M) thank the Atomic Energy Establishment, Bombay, for research fellowships

J Inorg Nucl Chem 1963 Vol 25 pp 201 to 203 Pergamon Press Ltd Printed in Northern Ireland

ORGANIC SALTS OF LANTHANIDE ELEMENTS—II

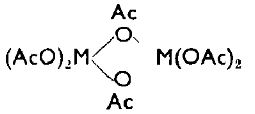
PREPARATION OF LANTHANUM AND CERIUM(III) ACYLATES FROM A NON-AQUEOUS MEDIUM

S N MISRA, T N MISRA, R C MEHROTRA*
Chemical Laboratories, Gorakhpur University, Gorakhpur India

(*Received* 24 *July* 1962)

Abstract The reactions of anhydrous lanthanum and cerium(III) chlorides have been studied with acetic acid, acetic anhydride-acetic acid and acetic anhydride In all three reactions, tri-acetates are the final products in quantitative yield The molecular weights, determined ebullioscopically in benzene show them to be monomeric Reactions of lanthanum and cerium(III) chlorides with palmitic acid have also been studied at different molar ratios in benzene and the mono-, di-, and tri-palmitates have been isolated

IN an earlier publication,(1) the preparation of the tri-laurates, palmitates, and stearates of lanthanum and cerium(III) has been described and they have been shown to be stable, non-hydrolysable compounds In a recent detailed study(2) the reactions of lanthanum and neodymium oxides with acetic acid and acetic anhydride have been shown to yield oxo-acetates with the formula $(AcO)_2M{-}O{-}M(OAc)_2\cdot 2AcOH$, which are converted to the tri-acetates only on prolonged refluxing with acetic anhydride These tri-acetates have been given bridge structure of the type



on the basis of their behaviour in conductometric titrations with acids Oxy-acylates of this type have been reported in the case of titanium(3) from the reactions of titanium oxide alkoxide as well as titanium alkoxides and titanium tetrachloride A similar detailed study in these laboratories(4) of the reaction of alkyl borates with acetic anhydride has confirmed the bridged structure of boron acetate reported by GERRARD(5) and by LAUBENGAYER(6) and co-workers

In view of the formation of non-hydrolysable cerium(III) and lanthanum soaps(1) from aqueous solutions and the formation of oxy-acetate products reported by STATON *et al.*(2), it was considered worth while to study the reactions of lanthanum and cerium (III) chlorides with palmitic acid in a non-aqueous medium It was found that these reactions are slow, more so in lanthanum chloride than in cerium(III) chloride but the mono- di-, and tri-palmitates can be isolated by simple metathetic reactions, e g

$$MCl_3 + xRCOOH \rightarrow MCl_{(3-x)}(RCOO)_x + xHCl$$

---

* *Present address* University Prof and Head of Chemistry Dept University of Rajasthan, Jaipur (India)

(1) S N MISRA T N MISRA and R C MEHROTRA, *J Inorg Nucl Chem* **25**, 195 (1963)
(2) J A STATON F G SHERIF and L F AUDRIETH, *J Inorg Nucl Chem* **9**, 222 231 (1955)
(3) K C PANDE and R C MEHROTRA, *Chem and Ind*, 114 (1957)
(4) A K RAI and R C MEHROTRA, Private communication (1962)
(5) W GERRARD and A M WHEELANS, *Chem and Ind* 758, (1954)
(6) R G HAYTER, A W LAUBENGAYER and P G THOMPSON, *J Amer Chem Soc* **79**, 4043, (1957)

(M = lanthanum or cerium(III), x = 1, 2 or 3) The formation of an oxygen-bridged compound could not be detected at any stage in the above reactions In view of their formation in the reaction between titanium tetrachloride and acetic acid, it was considered of interest to study the reaction between anhydrous lanthanum and cerium(III) chloride and acetic acid, acetic acid acetic anhydride mixture and acetic anhydride In all these cases quantitative yields of the tri-acetates were obtained as final products Measurements of the molecular weights of these compounds in benzene showed them to be monomeric, in sharp contrast to the bridged structure suggested on the basis of their physico-chemical properties

EXPERIMENTAL

Material

Anhydrous acetic acid (E Merck) was dehydrated by refluxing with acetic anhydride(2) followed by fractionation Acetic anhydride (B D H) was purified by fractionation and the distillate collected at 138 140 C Palmitic acid (B D H) was purified by distillation under reduced pressure Benzene (B D H) was purified as in our earlier work(1)

Anhydrous lanthanum chloride, prepared from lanthanum oxide (E Merck, 99 per cent), was dissolved in hydrochloric acid (A R) and evaporated to dryness This process was repeated four times and the anhydrous salt was prepared by heating in a closed tube in dry hydrogen chloride Anhydrous cerium(III) chloride was obtained from a hydrated sample (B D H) by removing the water azeotropically with benzene and ethanol The final product was freed from volatile solvents under reduced pressure

Methods

Molecular weights were determined ebullioscopically in dry benzene as in Part I(1)

Analyses

Lanthanum and cerium(III) in the acetates were estimated by igniting a weighted quantity at 900 C to the respective oxides Carbon and hydrogen contents of the acetates were estimated by standard methods In the chloride acylates, lanthanum and cerium were estimated by precipitation as the oxinates

Preparation of chloride acylates of lanthanum and cerium(III)

(i) *Reaction of lanthanum chloride and palmitic acid* (*molar ratio* 1 1) Freshly-distilled palmitic acid (1 294 g) was added to powdered anhydrous lanthanum chloride (1 25 g) in 30 g of dry benzene, and the contents were refluxed After several hours refluxing evolution of hydrogen chloride gas had not stopped completely, although it had become very slow The product was filtered and washed repeatedly with dry methanol in which both lanthanum chloride and palmitic acid are soluble After washing, the compound was dried under reduced pressure (0 05 mm) at 30 C for 3 hr (Yield 1 506 g Found La 30 49, Cl, 16 28 Calc for $La(C_{15}H_{31}COO)Cl_2$ La, 30 1, Cl, 15 24%)

(ii) *Reaction of cerium*(III) *chloride and palmitic acid* (*molar ratio* 1 1) Cerium (III) chloride (1 34 g), palmitic acid (1 33 g) and benzene (30 g) were refluxed in a bath at 110 C The compound was filtered and washed several times with dry methanol, dried under reduced pressure and analysed (Yield 1 29 g Found Ce, 30 49, Cl, 16 4 Calc for $Ce(C_{15}H_{31}COO)Cl_2$ Ce, 29 95, Cl, 15 2%)

(iii) *Reaction of lanthanum chloride and palmitic acid* (*molar ratio* 1 2) Lanthanum chloride (1 489 g), palmitic acid (3 304 g) and benzene (25 g) were refluxed at a bath temperature of 110 C Hydrogen chloride was not detected before 8 hr refluxing The reaction was stopped after several hours and the product filtered, washed thoroughly with dry methanol, and dried under reduced pressure (0 05 mm) at 30°C (Yield 1 89 g Found La, 21 2, Cl, 4 8 Calc for $La(C_{15}H_{31}COO)_2Cl$ La, 20 4, Cl, 5 18%)

(iv) *Reaction of cerium* (*III*) *chloride and palmitic acid* (*molar ratio* 1 2) Cerium(III) chloride (1 35 g), palmitic acid (2 70 g) and benzene (35 g) were refluxed in a bath at 115 C and after 15 hr refluxing hydrogen chloride was detected at the top of the condenser After prolonged refluxing a glassy solid separated from the lower, unreacted cerous chloride Refluxing was continued until the evolution of hydrogen chloride had slowed down considerably The compound was filtered through a sintered funnel (G-4), washed thoroughly with methanol, and dried under reduced pressure (Yield 1 28 g Found Ce, 20 8, Cl, 5 4 Calc for $Ce(C_{15}H_{31}COO)_2Cl$ Ce, 20 36, Cl, 5 14%)

(v) *Reaction of lanthanum chloride and palmitic acid* (*molar ratio* 1 3) Finely powdered lanthanum chloride (1 0 g), freshly-distilled palmitic acid (3 10 g) and anhydrous benzene (30 0 g) were refluxed in a bath kept at 115°C for several hours It was evident from the speed of evolution of hydrogen chloride that this reaction was faster than those with 1:1, and 1:2 molar ratios. After several hours' refluxing the reaction was terminated when evolution of hydrogen chloride gas had ceased. The compound was filtered, washed several times with methanol, and dried under reduced pressure (0.05 mm) at 30°C. (Yield: 2.01 g. Found: La, 16.3; $C_{15}H_{31}COO$ (palmitate), 83.5. Calc. for $La(C_{15}H_{31}COO)_3$: La, 15.54; $C_{15}H_{31}COO$, 84.46%.)

(vi) *Reaction of cerium(III) chloride with palmitic acid (molar ratio 1:3).* Cerium(III) chloride (1.63 g), palmitic acid (5.19 g) and benzene (30 g) were refluxed at a bath temperature of 115°C for several hours. The reaction was terminated after several hours' refluxing. The product was filtered, washed repeatedly with dry methanol, and dried under reduced pressure. (Yield: 3.25 g. Found: Ce, 14.98; $C_{15}H_{31}COO$ (palmitate), 84.3. Calc. for $Ce(C_{15}H_{31}COO)_3$: Ce, 15.48; $C_{15}H_{31}COO$, 84.52%.)

Preparation of rare earth acetates

(i) *Reaction of lanthanum chloride and acetic acid.* Lanthanum chloride (2.34 g) and acetic acid (60 g) were refluxed on an oil bath (135°C) for several hours. Hydrogen chloride was detected at the top of the condenser just after refluxing had started. The evolution of hydrogen chloride was very rapid initially, but gradually became slower. After half an hour the lanthanum chloride had dissolved completely in the solvent, and after a few hours' refluxing a white crystalline solid separated from the solution. When reaction was complete as shown by the absence of hydrogen chloride at the top of the condenser the product was filtered, washed several times with dry acetic acid and dried under reduced pressure at 70°C. (Yield: 2.98 g. Calc. yield: 3.02 g. Found: La, 43.89; C, 22.84; H, 2.90. Calc. for $La(CH_3COO)_3$: La, 44.11; C, 22.74; H, 2.86%.)

(ii) *Reaction of cerium(III) chloride and acetic acid.* Cerium(III) chloride (2.53 g) acetic acid (30 g) were refluxed in an oil-bath (135°C), the reaction began immediately with vigorous evolution of hydrogen chloride. As refluxing proceeded a white solid separated. When the reaction was complete this was filtered, washed thoroughly with acetic acid, and dried at 60°C under reduced pressure. (Yield: 2.73 g. Calc. yield: 2.8 g. Found: Ce, 44.4; C, 22.8; H, 2.85. Calc. for $Ce(OOCCH_3)_3$: Ce, 44.16; H, 2.85; C, 22.7%.)

(iii) *Reaction of lanthanum chloride with acetic acid acetic anhydride.* Acetic acid (30 g), acetic anhydride (30 g) and lanthanum chloride (3.28 g) were refluxed an oil-bath for several hours. It was only after 4 hr refluxing that hydrogen chloride was detected, indicating that this reaction was slower than that with acetic acid. Once reaction had begun, hydrogen chloride was liberated at an appreciable rate and the reaction was complete after several hours. The solid, which started to separate as soon as the reaction had commenced, was filtered, washed thoroughly with acetic acid and acetic anhydride and dried at 70°C under reduced pressure. (Yield: 4.1 g. Calc. yield: 4.22 g. Found: La, 44.3; C, 22.75; H, 2.91. Calc. for $La(OOCCH_3)_3$: La, 44.11; C, 22.76; H, 2.85%.)

(iv) *Reaction of cerium(III) chloride with acetic acid–acetic anhydride.* Cerium(III) chloride (3.42 g), acetic acid (30 g) and acetic anhydride (30 g) were refluxed for several hours in a bath at 130°C. On prolonged refluxing the chloride dissolved, but on cooling a crystalline solid separated in amounts which increased with increasing time of refluxing. After completion of the reaction the solid was filtered, washed thoroughly with acetic anhydride-acetic acid and dried under reduced pressure at 65°C. (Yield: 4.34 g. Calc. yield: 4.5 g. Found: Ce, 44.34; C, 22.74; H, 2.94. Calc. for $Ce(OOCCH_3)_3$: Ce, 44.16; C, 22.75; H, 2.85%.)

(v) *Reaction of lanthanum chloride and acetic anhydride.* Lanthanum chloride (2.18 g) and acetic anhydride (60 g) were refluxed for several hours, hydrogen chloride was only detected after 10 hr refluxing, dissolution of lanthanum chloride was also slower in this case. When hydrogen chloride was no longer detectable the product was filtered, washed thoroughly with acetic anhydride and dried under reduced pressure at 70°C. (Yield: 2.75 g. Calc. yield: 2.80 g. Found: La, 44.3; C, 22.95; H, 2.75. Calc. for $La(OOCCH_3)_3$: La, 44.11; C, 22.76; H, 2.85%.)

(vi) *Reaction of cerium(III) chloride with acetic anhydride.* Cerium(III) chloride (3.14 g), and acetic anhydride (40 g) were refluxed at a bath temperature of 140°C for several hours. This reaction was also slow and hydrogen chloride could only be detected after 9 hr refluxing. The product was filtered, washed with acetic anhydride several times, and dried under reduced pressure at 65°C. (Yield: 3.94 g. Calc. yield: 4 g. Found: Ce, 44.38; C, 22.98; H, 2.7. Calc. for $Ce(OOCCH_3)_3$: Ce, 44.16; C, 22.75; H, 2.85%.)

Acknowledgement—Two of us (S. N. M., T. N. M.) are grateful to the Atomic Energy Establishment, Bombay, for the award of research fellowships.

J. Inorg. Nucl. Chem. 1963. Vol. 25, pp. 205 to 213. Pergamon Press Ltd. Printed in Northern Ireland

THE EFFECT OF ADDITIVES AND STABILIZERS ON THE EXTRACTION BEHAVIOUR OF U(VI) AND Pu(IV) NITRATES WITH TERTIARY AMINES

F. Baroncelli, G. Scibona and M. Zifferero
C.N.E.N.
Laboratorio Trattamento Elementi Combustibili c/o Istituto di Chimica
Farmaceutica dell'Università di ROMA

(*Received* 14 *December* 1961; *in revised form* 7 *June* 1962)

Abstract—The use of additives and stabilizers in the solvent extraction of actinides with tertiary amines to control the third phase formation and the Pu valence state introduces new variables in the solvent extraction behaviour of these elements. The effect of the separate presence of nitrous acid as a stabilizer and of a long chain aliphatic alcohol as an additive has been evaluated for uranyl and plutonium nitrate.

Depending on the acidity of the aqueous solution the addition of nitrite to the water phase can depress or enhance the partition coefficients. The addition of a long chain alcohol has only a depressing effect. When the additive and the stabilizer are present at the same time, the partition coefficient is a maximum when equal molar concentration of alcohol and nitrous acid are added to the organic phase. A coherent interpretation of this behaviour is given.

The use of tertiary amine salts dissolved in a suitable diluent as potential extractants in the reprocessing of irradiated nuclear fuels is well known.(1, 2) Lately, an increasing number of works has been published on the extraction behaviour of the actinides in the nitrate systems(2, 3, 4) and hypotheses have been advanced on the extraction mechanism.(5, 6)

The choice of a suitable diluent and the need for additives arise from the fact that the amine–acid complexes and the amine–actinide complexes have sometimes limited solubility in the diluent and when this is exceeded the organic solution splits into two phases.

It has been shown that aromatic diluents such as toluene or xylene are preferable to aliphatic hydrocarbons because they yield more stable solutions;(7) the use of small quantities of long chain aliphatic alcohols as additives to the extracting system has proved beneficial because it increases the solubility of the amine complexes in the diluent.(7) The same effect is obtained with an increase in temperature.(7, 8)

No information so far has appeared on the effect of the presence of such additives in the organic solvent phase on the extraction behaviour of uranium and plutonium.

Furthermore, the recovery of plutonium from irradiated fuels generally utilizes

---

(1) A. S. Wilson—*The Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy*—*Geneva* 1958. P/544 Vol. 17 p. 348. United Nations (1958).

(2) W. E. Keder, J. C. Sheppard and A. S. Wilson, *J. Inorg. Nucl. Chem.* **12**, 327 (1960).

(3) B. Weaver and D. E. Horner, *J. Chem. Engng. Data*, **5**, 260 (1960).

(4) F. Baroncelli and M. Zifferero, CNC-41 (July 1960).

(5) F. Baroncelli, G. Scibona and M. Zifferero, *J. Inorg. Nucl. Chem.* **24**, 405 (1962).

(6) F. Baroncelli, G. Scibona and M. Zifferero, *J. Inorg. Nucl. Chem.* **24**, 541 (1962).

(7) K. B. Brown, C. F. Coleman, D. J. Crouse, J. O. Denis and J. G. Moore, AECD 4142 (1954).

(8) J. E. Jenkins and A. G. Wain, AERE-M537 (1959).

[illegible] the fundamental [illegible] [illegible] ions and are present [illegible] [illegible] The presence of nitrite ions is in [illegible]

TABLE 1 — HNO_2 EXTRACTION IN SOLVESSO 100 VS NONANOL CONCENTRATION

Initial aqueous phase 1.0 M HNO_3, 0.22 M HNO_2 Organic phase Solvesso 100 with varying concentrations of nonanol Phase ratio o/a 2.5

R–OH molarity in Solvesso 100	NO M aq phase at equil	HNO_2 M org phase at equil
0	0.179	0.080
0.058	0.137	0.166
0.115	0.100	0.245
0.173	0.055	0.352
0.288	0.021	0.457
0.576	0.003	0.502
0.835	0.001	0.510

order to stabilize Pu in the tetravalent state, which is the only one suitable for extraction The addition of nitrite ions prior to each extraction is necessary if further extraction cycles are used

Again no data are available on the influence of nitrous acid on the extraction behaviour of plutonium and uranium only some information exists on the extraction behaviour of nitrous acid in triisononyl amine nitrate in xylene (9)

The purpose of this work was to investigate the effect of such stabilizers and additives on the extraction behaviour of U and Pu into tertiary amine nitrate diluent solutions The following systems have been studied

(a) Diluent–HNO_2
(b) Diluent additive HNO_2
(c) Amine diluent HNO_2
(d) Amine diluent additive HNO_2
(e) Amine–diluent HNO_2 + U, Pu
(f) Amine–diluent additive + U, Pu
(g) Amine–diluent additive HNO_2 + U, Pu

Marked effects have been noticed on the extraction behaviour of U and Pu in presence of additives or stabilizers or both

EXPERIMENTAL

Several tertiary amines have been considered a list including sources and formula is given in Reference (6) Solvesso 100, principally a mixture of trimethylbenzene isomers, an aromatic industrial naphtha, was mainly used as diluent, only in certain cases was xylene (mixture of isomers, reagent grade) preferred 3-5-5-trimethylhexan-1-ol, a commercial grade nonylalcohol, was used as the additive All other chemicals were reagent grade Plutonium nitrate was purified from americium as described elsewhere (11) The extraction procedures, the preparation of the amine salt solution and of the labeled uranyl nitrate have been described before (1, 6) All the extractions were carried out at room temperature The nitrous acid was determined by the standard ceric ammonium nitrate titration (12)

(9) U Bertocci, AERE-R2933 (1959)

(10) K Singer and P A Vamplew, *J Chem Soc* 3971 (1956)

(11) F Baroncelli, G Scibona and M Zifferero, *J Inorg Nucl Chem* **24**, 547 (1962)

(12) F M Stubblefield, *Industr Engng Chem Analyt Ed* **16**, 366 (1944)

RESULTS AND DISCUSSION

Case (a) and (b)

The partition of HNO_2 between an aqueous phase containing HNO_3 and $NaNO_2$ and an organic phase consisting of the diluent alone and then with varying amounts of nonanol was first investigated. The results of extraction experiments are collected in Table 1.

Nitrous acid is moderately soluble in the pure diluent. The addition of the alcohol to the diluent increases the extraction of HNO_2 into the organic phase. This increase appears to be approximately proportional to the nonanol concentration, suggesting the formation of an $R\,OH\text{-}HNO_2$ complex. Above 5 per cent nonanol the experimental conditions are such that practically all the nitrous acid is extracted into the organic phase.

Case (c)

Nitrous acid is extracted into Solvesso solutions of tertiary amine nitrate as a linear function of the amine concentration. The results of the extraction experiments are plotted in Fig. 1. Aqueous nitrous acid solutions show absorption at 356, 371 and 385 mμ[10]. In the organic phase absorption maxima are observed at 338, 348, 360, 375 and 390 mμ. The absorption at 338 and 348 mμ is probably associated with a labile nitrogen oxide, the peaks vanish on ageing the solutions.

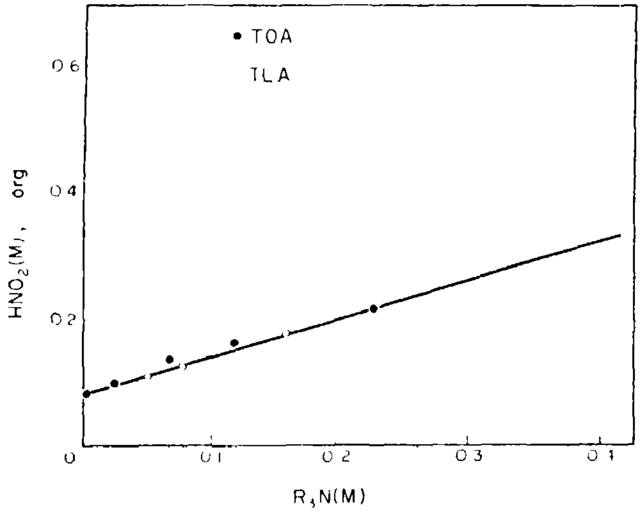


FIG. 1. The extraction of HNO_2 by Solvesso solutions of tri-n-octylamine nitrate and tri-n-dodecylamine nitrate (TLA) versus amine concentration. Initial aqueous phase 0.22 M $NaNO_2$. Equilibrium aqueous phase 1.6 M HNO_3.

HNO_2 solutions in Solvesso-nonanol as under case (b) show sharp absorption a 345, 355 and 370 mμ plus a slight absorption at 335. This latter peak and the shift of the maxima are probably associated with the postulated HNO_2-nonanol complex.

Case (d)

The absorption spectra of $TLAHNO_3$ diluent solutions containing HNO_2 are modified when nonanol is added. This modification is probably related to the formation of the nonanol HNO_2 complex mentioned under case (b).

Case (c)

The acid dependence of $E_{U(VI)}$ and $E_{Pu(IV)}$ is described in Fig. 2 in absence of additives or stabilizers. If $NaNO_2$ is gradually added to an aqueous phase initially 4 M in HNO_3 and containing uranium or plutonium, the partition coefficient in the extraction with TLA·HNO_3 diluent decreases with increasing nitrite molarity as shown in

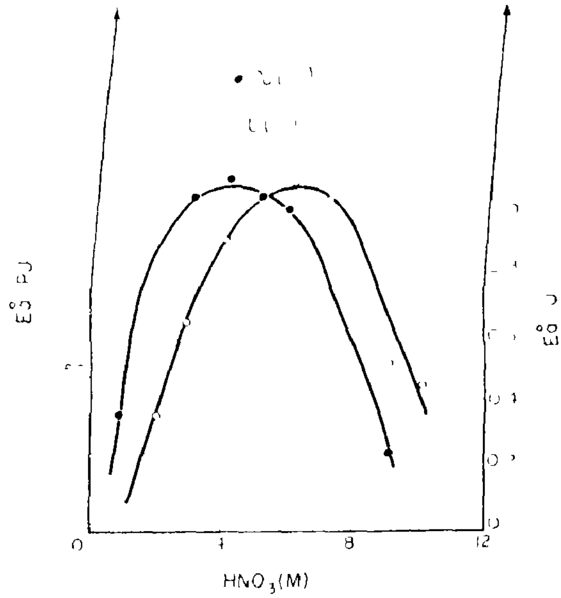


Fig. 2 — The extraction of plutonium nitrate and uranyl nitrate by 10 v/o TLA nitrate in xylene. Initial aqueous conditions: 0.5 g U/l and 0.1 g Pu/l.

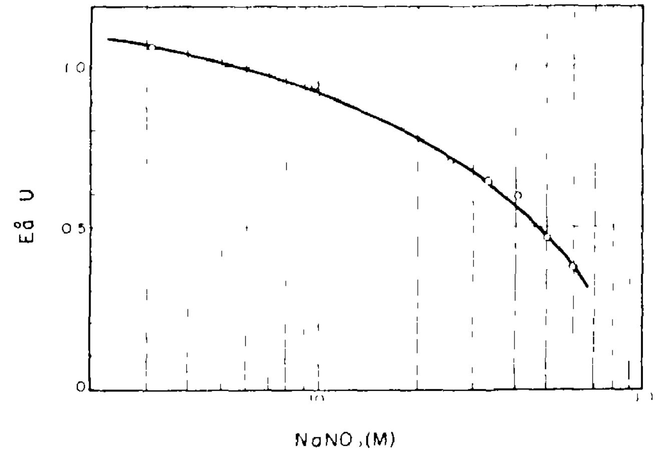


Fig. 3 — The effect of the addition of sodium nitrite on the extraction of uranyl nitrate by 10 v/o TLA nitrate in xylene. Initial aqueous phase 4 M in HNO_3.

Fig. 3 and 11. This is due to the consumption of HNO_3, caused by the addition of $NaNO_2$ through the formation of HNO_2, in agreement with the acid dependence of E_{Pu} and E_U.

This behaviour is inverted (Fig. 5) if the initial aqueous HNO_3 molarity is nine. If the partition coefficient of U between aqueous phase and solid anion exchange resin is plotted versus $NaNO_2$ molarity (Fig 4) a similar curve is obtained confirming the analogy between anion exchangers and tertiary amines, already reported ⁽⁶⁾

The variation of E_{Pu} and E_U in the above mentioned experimental conditions suggests that the HNO_2 extraction into the organic phase is not accompanied by a corresponding back extraction of HNO_3 from the organic into the aqueous phase, in which case the aqueous HNO_3 molarity would remain unchanged from the equilibrium value

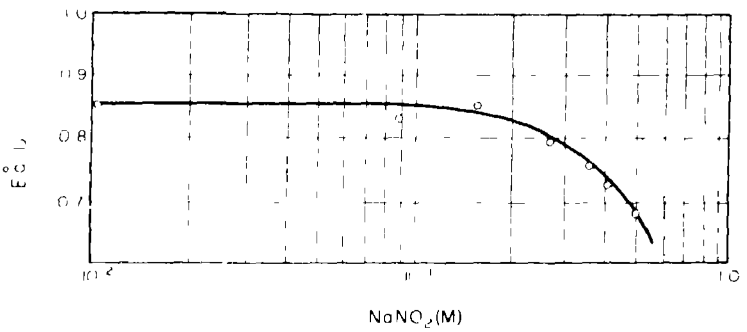


Fig. 4—Effect of the addition of $NaNO_2$ on the partition coefficient of uranyl nitrate between an initially 4 M nitric acid solution and Dowex 1 (nitrate form–200 400 mesh)

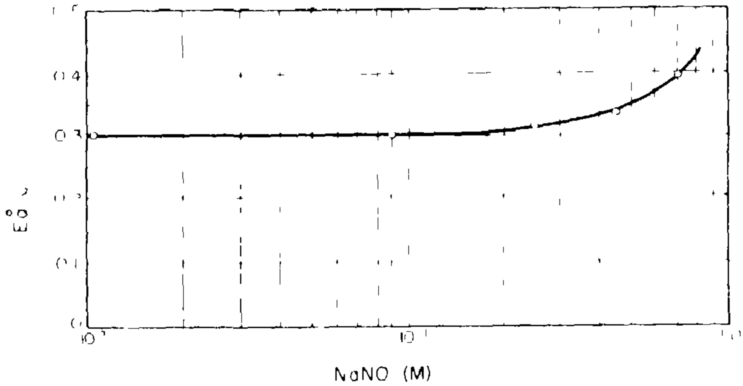


Fig. 5 The effect of the addition of $NaNO_2$ on the extraction of uranyl nitrate by 10% TLA nitrate in xylene Initial aqueous phase 9 M in HNO_3

Case (f)

The addition of nonanol to the amine nitrate diluent system enhances the extraction of nitric acid into the organic phase as shown in Fig 6

The quantity of nitric acid extracted is a linear function of the nonanol concentration The value of the intercept at 0 per cent nonanol actually corresponds to the expected HNO_3 concentration⁽¹¹⁾ in a 10 v/o TLA-xylene system

The additional nonanol increases the concentration of nitric acid in the organic phase The observed E_{Pu} and E_U decrease (Fig 7) This is probably due at least in part to the increased dielectric constant of the organic phase in the presence of excess nitric acid

It has been shown previously⁽⁶⁾ that solid uranyl nitrate (UNH) is soluble in solutions of amine nitrate diluent The resulting uranium loaded organic system contains the same trinitratouranyl complex which is obtained by extraction of uranium from an aqueous solution. This fact permits the study of the influence of the organic phase composition on *the formation of the uranium complex in the absence of a water phase. In the present case the solubility of solid ^{233}U labeled UNH in an organic phase containing various concentrations of nonanol was studied.* *

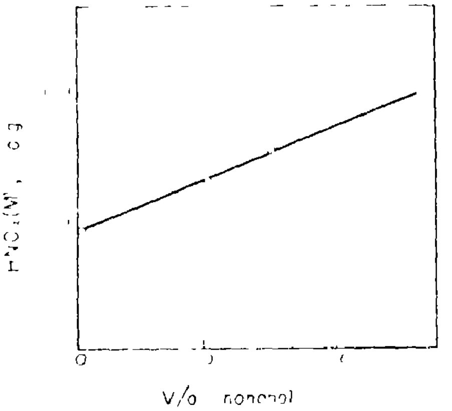


FIG. 6. Effect of nonanol on the extraction of nitric acid (initially 6 M) by 10 v/o TLA nitrate in xylene.

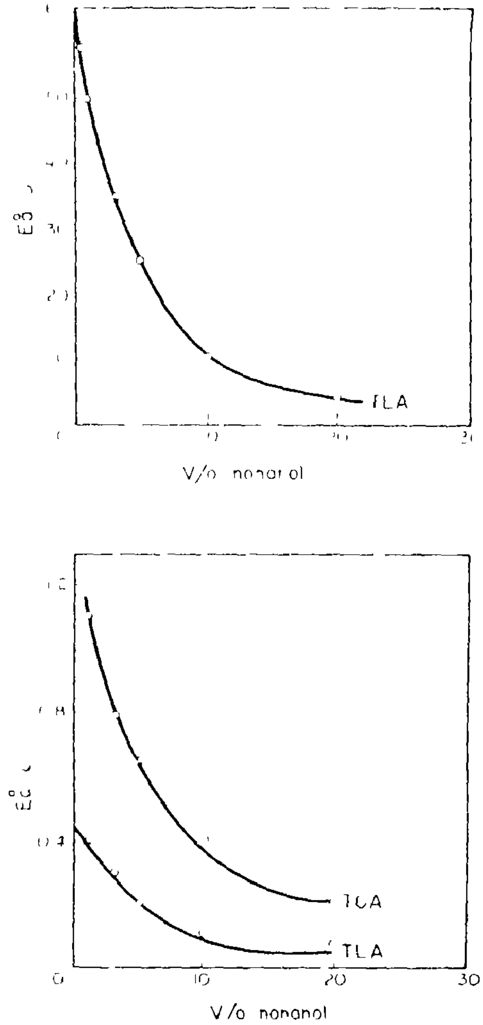


FIG. 7.—The effect of nonanol on the extraction of uranyl nitrate and plutonium nitrate by 10 v/o amine nitrate from 4 M nitric acid.

Results were plotted in Fig. 8. The solubility of solid UNH is a linear function of the percent nonanol; if the HNO_3 concentration is also increased in such a way that the ratio HNO_3/nonanol is held constant the effect on the solubility is given by the dotted line.

The slope of the latter function is lower indicating that a simultaneous increase of the nitric acid and nonanol concentration has a depressing effect on the solubility of

---

* Solid UNH is readily soluble in nonanol-diluent systems.

UNH Previous experiments had shown that the solubility of UNH in the TLAHNO$_3$–diluent system (without nonanol) was not affected by varying concentrations of nitric acid (6)

The results of the UNH solubility experiments are coherent with those obtained from liquid liquid extraction While the increased solubility in the organic phase with increasing nonanol would not agree with the observed depression of the organic/aqueous partition coefficient, the effect of added nitric acid on depressing the increase of solubility induced by nonanol is consistent with the observed partition coefficients In extraction experiments the nonanol addition is accompanied by nitric acid extraction into the organic phase

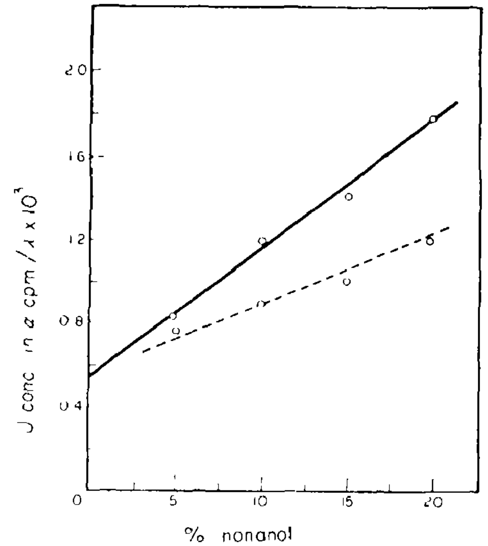


Fig 8 – Effect of nonanol on the solubility of solid uranyl nitrate in 10 v/o TLA nitrate in xylene at constant HNO$_3$ concentration in the solvent (solid line), at constant HNO$_3$/nonanol in the solvent (dotted line)

Usually a log log plot of the partition coefficient of a metal vs the free amine concentration is a straight line with a slope which gives information on the composition of the amine metal complex In fact, the numerical value of the slope corresponds to the amine/metal ratio in the complex Thus this ratio is two for the amine-plutonium complex (2 9) and approximately 1 5 for the amine–uranium complex (2 6)

The presence of a constant amount of additive in the organic phase modifies the values of the slopes (Table 2 and Fig 9) This behaviour is important only at high nonanol/amine ratio (i e low concentration of free amine)

This fact should be born in mind when performing experiments of this kind because if an additive is present in the organic phase, the meaning of the slope is lost However, if the amine/nonanol ratio is kept constant the log-log plot of the partition coefficient vs the amine concentration is a straight line with a slope which is essentially independent of the actual value of the ratio

Case (g)

The depressing effect of the nonanol (Fig 7) on the L_{Pu} and L_U as indicated under case (f) is neutralized by the presence of HNO$_2$ in the organic phase This is shown in

TABLE 2 VALUES OF THE SLOPES IN THE LOG-LOG PLOT OF THE U AND Pu PARTITION COEFFICIENT VERSUS AMINE CONCENTRATION AT CONSTANT ACIDITY AND VARYING NONANOL CONCENTRATION

Nonanol concentration	E_U	E_{Pu}
0 v/o	1 4	2 0
5 v/o	1 8	2 9
nonanol/amine 2	1 1	2 0

aq ^{233}U 0 5 mg ml (HNO_3 6 M)
Pu 0 1 mg/ml (HNO_3 4 M)
org varying conc of TLAHNO$_3$ in xylene

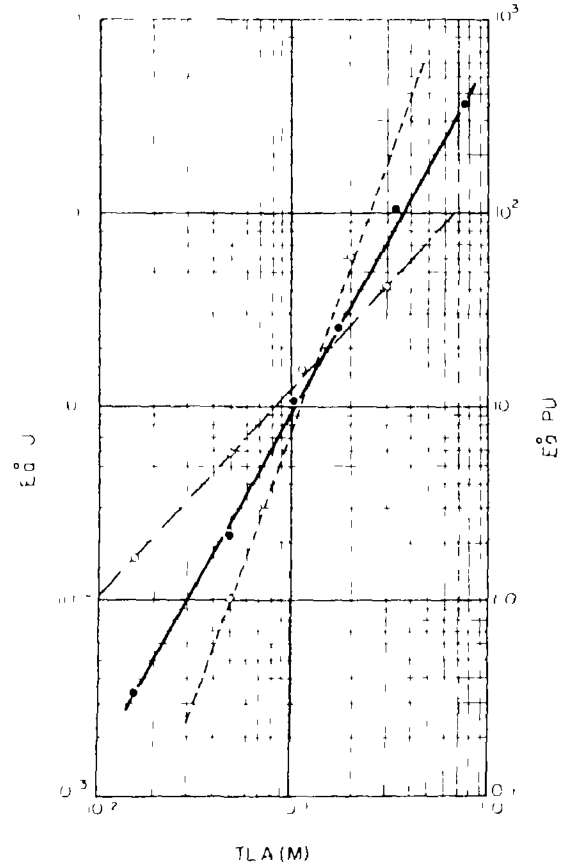


FIG 9 Extraction of plutonium nitrate and uranyl nitrate by TLA nitrate in xylene from 4 M nitric acid

●— U extraction 5 v/o nonanol added to the organic phase

● ● U extraction The ratio amine/nonanol is kept constant $\frac{\text{v/o amine}}{\text{v/o nonanol}}$ 2

Pu extraction 5 v/o nonanol added to the organic phase

Figs 10 and 11 where E_U and E_{Pu} respectively are plotted versus $NaNO_2$ concentration in the aqueous phase at constant acidity and for different values of nonanol concentration Each curve of both families is characterized by a maximum when the $NaNO_2$/nonanol molar ratio is near one The presence of this maximum is coherent with the interpretation given under case (b), (e) and (f) Separately considered at 4 M HNO$_3$, both nonanol and nitrous acid have a depressing effect on E_U and E_{Pu}, when they are present at the same time some complex between the alcohol and nitrous acid is

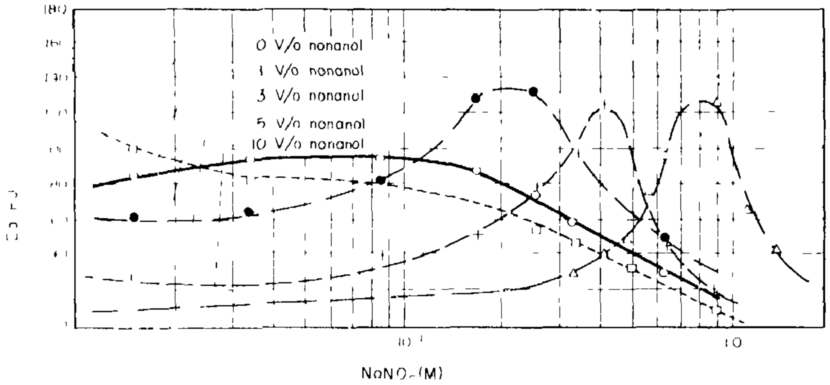


FIG. 10 — The effect of nitrous acid on the extraction of plutonium nitrate from 4 M nitric acid by 10 v/o TLA nitrate in Solvesso Each curve refers to a different value of nonanol concentration

probably formed From the curves in Fig 11 it can be inferred that the complex has much less effect on the partition coefficient of uranium than with nonanol or sodium nitrite added separately In the case of plutonium the simultaneous presence of appropriate concentrations of nitrous acid and nonanol increases significantly the

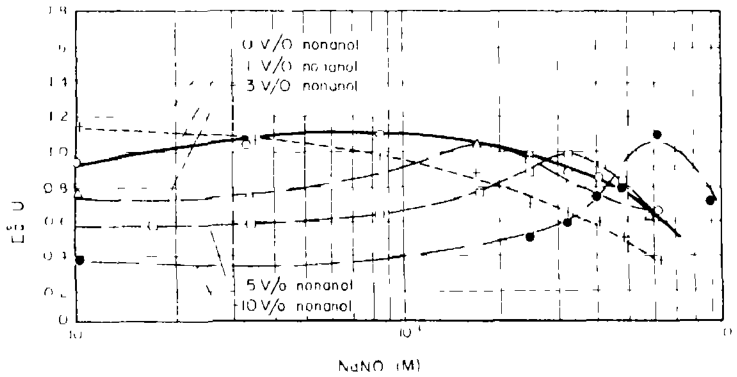


FIG. 11 The effect of nitrous acid on the extraction of uranyl nitrate from 4 M nitric acid by 10 v/o TLA nitrate in xylene Each curve refers to a different value of nonanol concentration

plutonium extraction (Fig 10) Five commercial amines* all exhibited this increase, indicating a possibly general phenomenon of long chain tertiary amines Experiments are in progress to obtain information on the behaviour of the most important fission products in presence of additives and stabilizers

Acknowledgement—We are indebted to Prof G GIACOMELLO for helpful discussions We wish to thank Messrs D FILONI, G B BIONDI, P SUSINI, R CARIGLIA and S ILARDI for their contribution in the experimental part

---

* Trilaurylamine (Rhone et Poulenc), tri-iso-octylamine (Union Carbide), tri-n-octylamine (Fluka) Alamine 336 (General Mills) and tri-n-octylamine (Chemical Procurement Co)

J. Inorg. Nucl. Chem. 1963. Vol. 25. pp. 215 to 228. Pergamon Press Ltd. Printed in Northern Ireland

NOTES

Copper (II) cyclopropane-1: amino-1: carboxylate and cyclobutane 1: amino-1: carboxylate

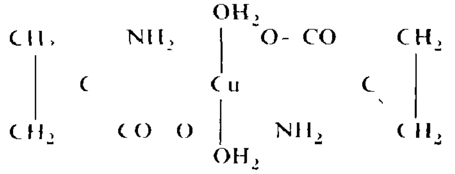
(*Received* 14 *March* 1962)

PREVIOUSLY we have discussed the relationship between adsorption spectra in the visible region and environment of the copper atom in a series of copper(II) α-amino-acid chelates,[1] and suggested that the unusual violet colour of anhydrous copper(II) α-amino-isobutyrate and cyclopentane-1 amino 1 carboxylate could be attributed to planar 4 co-ordination of the copper atoms in these compounds in the solid state. This prediction has since been confirmed by X-ray analysis of the cyclopentane-1 amino-1 carboxylate, the nearest atoms to copper in the direction normal to the molecular plane being carbonyl oxygen atoms of neighbouring molecules at a distance of 3.2 Å U.[2]

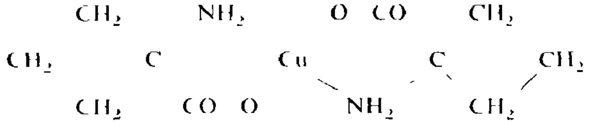
We now report absorption spectra in the solid state and in aqueous solution of copper(II) cyclopropane-1 amino-1 carboxylate and cyclobutane-1 amino-1 carboxylate.

Copper(II) cyclopropane-1 amino-1 carboxylate crystallizes from aqueous solution as the blue monohydrate, the cyclobutane-1 amino-1 carboxylate crystallized anhydrous in violet plates. Absorption spectra of the solid compounds are shown in Fig. 1. Both substances are freely soluble in water giving blue solutions, the absorption spectra of which are also shown in Fig. 1.

We conclude that, in aqueous solution both compounds are present as molecular species, in which 6 co-ordination of the copper atoms is completed by water molecules (I). A similar environment of the copper atoms is preserved in the solid hydrated cyclopropane-1 amino-1 carboxylate, the shift in the absorption peak from 617 $m\mu$ in solution to about 632 $m\mu$ in the solid being related to the differing availability of water molecules. In solid, anhydrous copper(II) cyclobutane-1 amino-1 carboxylate however, we conclude that the copper atoms are 4 co-ordinated (II) as in the cyclopentane-1 amino-1 carboxylate and the α-aminoisobutyrate.



(I)



(II)

Discussion

Stability of 4 co-ordinated structures

Any planar 4 co-ordinated structure has the metal atoms exposed in such a way that it is inherently likely to accept further donor groups to extend the co-ordination number to five or six, numerous such additions have been observed with the planar compounds of nickel(II), palladium(II) and platinum(II). in the case of copper(II) 5 and 6 co-ordination are much more common than 4 co-ordination.

The present examples of 4 co-ordination appear to be due entirely to considerations of packing in the crystal lattice. there is clearly no possibility of obstruction of the fifth and sixth positions of the copper atom, our spectroscopic evidence is consistent with the extension of the co-ordination number to six in aqueous solution, and the observed 4 co-ordinated structure is highly stereospecific, being observed only in the cyclopentane-1 and cyclobutane-1 amino-1 carboxylates and the α-amino-isobutyrate. In this context some very much earlier observations of the colours of some copper(II) α-amino-alkanoates assume a new significance. thus, ZELINSKY and STADNIKOV in 1906[3] observed

---

[1] D. P. GRADDON and L. MUNDAY, *J. Inorg. Nucl. Chem.* **23**, 231 (1961).

[2] G. A. BARCLAY and E. S. STEPHENS, private communication.

[3] N. ZELINSKY and G. STADNIKOV, *Ber.* **39**, 1722 (1906).

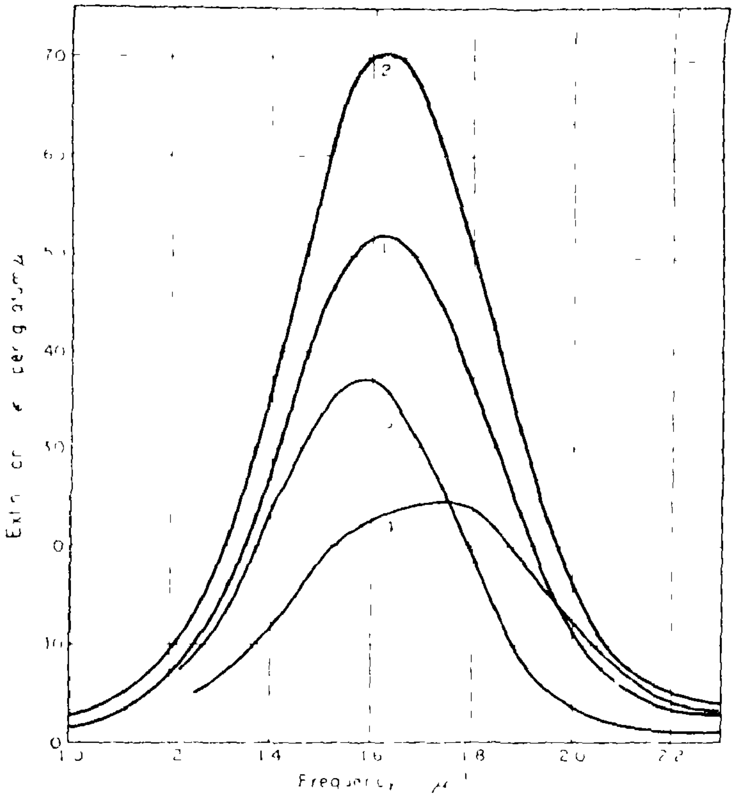


FIG. 1 Absorption spectra of (1) aqueous copper(II) cyclopropane-1 amino-1 carboxylate, (2) aqueous copper(II) cyclobutane-1 amino-1 carboxylate, (3) solid copper(II) cyclopropane-1 amino-1 carboxylate monohydrate, (4) solid copper(II) cyclobutane-1 amino-1 carboxylate anhydrous For the solid compounds the extinction scale is arbitrary

TABLE 1 —VISIBLE REGION ABSORPTION BANDS OF COPPER(II) CYCLIC α-AMINO-ACID CHELATES IN AQUEOUS SOLUTION

α-amino-acid	λ_{max} (mμ)	ν_{max} (μ^{-1})	ϵ
glycine	630	1.59	43
cyclopropane-1 amino-1 carboxylic	617	1.62	51
cyclobutane-1 amino-1 carboxylic	614	1.63	70
cyclopentane-1 amino-1 carboxylic	610	1.64	66
cyclohexane-1 amino-1 carboxylic	605	1.65	74
α-amino-isobutyric	617	1.62	70

that copper(II) 3 methylcyclopentane-1 amino-1 carboxylate crystallized from water anhydrous in violet plates (presumably another example of the 4 co-ordinated structure type) and that the cycloheptane-1 amino-1 carboxylate could be obtained in three different forms, depending upon the conditions of crystallization a violet anhydrous form (presumably 4 co-ordinated), a pale blue anhydrous form (probably with a structure of the α-amino-n-butyrate type) and a blue-violet hemihydrate This evidence clearly suggests that the cycloheptane ring marks the upper limit of tolerance for the 4 co-ordinated crystal structure

2. Absorption spectra of the cyclic compounds in aqueous solution

In aqueous solution all of our compounds have a single, apparently symmetrical, absorption band in the 600–650 mμ region, which we regard as characteristic of 6 co-ordinated molecules, such as I. Table 1 shows the wavelengths, frequencies and extinctions of these bands.

The distinct shift of the absorption band to shorter wavelength with increasing ring size might be attributable to the increasing inductive effect of the alkyl side chains on the orbital separation energy of the copper atom, but we should then expect a corresponding shift in the open chain compounds, which was not observed. It thus seems more probable that this shift should be attributed to the steric effect of increasing ring size in reducing the ligand-field of the water molecules in the fifth and sixth positions, thus leading to a successively increasing tetragonal distortion, which remains too small however, for the accompanying splitting of the absorption bands to be observed experimentally.

Experimental

Samples of the copper(II) chelates of cyclopropane-1 amino-1 carboxylic acid and cyclobutane-1 amino-1 carboxylic acid were provided by Drs. T. A. Connors and W. C. J. Ross, Chester Beatty Royal Cancer Research Hospital, London.

Analyses were determined on small samples of materials as follows:

	% C	% H	% N	% Cu
Copper(II) cyclopropane-1 amino-1 carboxylate monohydrate found	33.2	4.9	10.3	22.4
found $C_8H_{14}O_5N_2Cu$ requires	34.1	5.0	10.0	22.5
Copper(II) cyclobutane-1 amino-1 carboxylate, anhyd., found	40.1	5.4	9.7	22.0
$C_{10}H_{16}O_4N_2Cu$ requires	41.2	5.5	9.6	21.8

Absorption spectra were obtained as in part I.

Analyses for C, H, N by Dr. E. Challen, University of New South Wales.

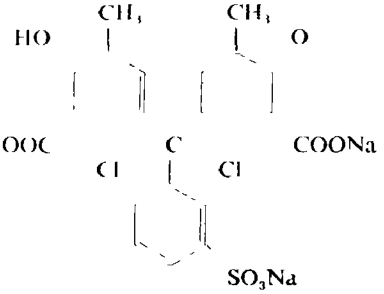
Inorganic Chemistry Department, University of New South Wales, Sydney, Australia D. P. Graddon

Technical College, Birkenhead, England I. Munday

The 1:1-beryllium(II) sulpho-dichloro hydroxy-dimethyl fuchson dicarboxylic acid chelate

(*Received* 16 *May* 1962, *in revised form* 18 *June* 1962)

Sulpho-dichloro hydroxy-dimethyl fuchson dicarboxylic acid (trisodium salt) Chrome Azurol S (CAS)



[illegible] has been used as a [illegible] metallochromic indicator[illegible] and colorimetric reagent[(9),(10)], but the [illegible] and [illegible] of its [illegible] chelates have not been reported upon. It forms very stable [illegible] chelates in solution with Cu(II), Be, Mg, Cd, [illegible], Ca(II), In(III), Zn(II), Th(IV), Mn(II), [illegible] Fe(III), Co(II), Ni(II) and Pd(II) under appropriate conditions. *This communication* gives the composition and stability of the 1:1-beryllium-CAS chelate and indicates its analytical possibilities.

Experimental

Solutions of $BeSO_4$ (BDH AnalaR) and C.A.S. (BDH indicator, trisodium salt, Colour Index 723) were prepared in doubly-distilled CO_2-free water. In view of the nature of the reagent as a colloidal electrolyte(11) solutions were $\leq 10^{-3}$ M. Absorbance measurements were carried out with a Unicam SP 500 Spectrophotometer against distilled water blanks.

Electrical conductances were measured with a Leeds and Northrup Kohlrausch slidewire with an audio-frequency oscillator and a dip-type cell. Hydrogen-ion concentrations were measured with a Leeds and Northrup direct-reading pH indicator. All experiments were carried out at 30 ± 0.01°C. The total volume of all the mixtures prepared for the measurements was kept at 50 ml. pH was adjusted to 6.0 ± 0.2 by addition of hydrochloric acid or sodium hydroxide, and ionic strength kept constant at 0.1 with sodium perchlorate.

The composition of the chelate was obtained by (i) the method of continuous variations(12) (using absorbance as well as electrical conductance measurements), (ii) the mole ratio method(13) and (iii) the slope ratio method(14) (both using absorbance measurements). The apparent stability constant was calculated from the absorbance data using the modified method of ANDERSON *et al.*(15, 16) as adopted by DEY and coworkers(17, 18, 19), and further corroborated by the mole ratio method as suggested by HARVEY and MANNING.(14)

Results and Discussion

Colour formation was instantaneous and the intensity remained constant for at least 72 hr. No appreciable change in observations was found to occur when the order of addition of the reagents was alternated.

The method of VOSBURGH and COOPER(20) was followed to determine the nature of the complexes formed in solution. The reagent alone shows a maximum absorption at 425 mμ at pH 6.0, while mixtures containing varying proportions of $BeSO_4$ and C.A.S. (1:0.5, 1:1, 1:2, 1:3 etc.) had λ_{max} at 540 mμ, showing that only one chelate is formed in solution under the conditions studied.

Table 1 summarizes the results from the method of continuous variations using absorbance measurements, and Fig. 1 shows typical measurements in one series.

Results obtained by the other methods mentioned above corroborate the composition of the chelate.

Measurements at different pH values and at various wavelengths indicate that the chelate is stable between pH 4.50 and 7.50, λ_{max} remaining constant within this range of pH. The colour intensity is maximum between pH 4.5 and 6.6. Values of log K determined by two different methods are in close agreement (Table 2).

---

(1) H. H. WILLARD and C. A. HORTON, *Analyt. Chem.* **22**, 1190 (1950).

(2) M. THEIS, *Z. Anal. Chem.* **144**, 106, 192, 275 (1955).

(3) A. MUSIL and M. THEIS, *Z. Anal. Chem.* **144**, 427 (1955).

(4) J. S. FRITZ and M. O. FULDA, *Analyt. Chem.* **26**, 1206 (1954).

(5) M. MALAT and M. TENOROVA, *Chem. Listy* **51**, (11), 2135 (1957).

(6) T. MATSUO, *Bunseki Kagaku* **7**, 557 (1958).

(7) S. P. SANGAL and A. K. DEY, *Z. Anal. Chem.* **178**, 415 (1961).

(8) D. RAVINSON and J. H. HARLEY, *Analyt. Chem.* **25**, 794 (1953).

(9) B. J. MACNULTY and L. D. WOOLLARD, *Anal. Chim. Acta* **14**, 452 (1956).

(10) L. SILVERMAN and M. E. SHIDELER, U.S.A.E.C. NAA-SR-2686, 21pp. (1958); *Analyt. Chem.* **31**, 152 (1959).

(11) S. C. SRIVASTAVA, R. L. SETH and A. K. DEY, *J. Colloid Sci.* **17**, 86 (1962).

(12) P. JOB, *C. R. Acad. Sci.* **180**, 928 (1925); *Ann. Chim.* (10) **9**, 113 (1928).

(13) J. H. YOE and A. L. JONES, *Industr. Engng. Chem. (Anal.)* **16**, 111 (1944).

(14) A. E. HARVEY and D. L. MANNING, *J. Amer. Chem. Soc.* **72**, 4488 (1950).

(15) R. C. ANDERSON and S. E. TURNER, *J. Amer. Chem. Soc.* **70**, 1195 (1948); **71**, 909 (1949).

(16) R. T. FOLEY and R. C. ANDERSON, *J. Amer. Chem. Soc.* **71**, 912 (1949).

(17) S. K. BANERJI and A. K. DEY, *Proc. Symp. Chem. Coord. Compounds Agra* 1959, **2**, 198 (1960).

(18) A. K. MUKHERJI and A. K. DEY, *J. Inorg. Nucl. Chem.* **6**, 314 (1958).

(19) A. K. MUKHERJI and A. K. DEY, *Anal. Chim. Acta* **18**, 324 (1958).

(20) W. C. VOSBURGH and G. R. COOPER, *J. Amer. Chem. Soc.* **63**, 437 (1941).

TABLE 1

Experiment	Curve	$c \times 10^4$ (M)	p	λ (mμ)	Volume of $BeSO_4$ (ml) at peak	Composition of the chelate Be : CAS
1 (Fig. 1)	A	3.33	1.00	540	25.0	1 : 1
	B	2.50	1.00	540	25.0	1 : 1
	C	2.00	1.00	540	25.0	1 : 1
2	A	3.33	1.00	525	25.0	1 : 1
	B	2.50	1.00	525	25.0	1 : 1
	C	2.00	1.00	525	25.0	1 : 1
3	A	5.00	0.66	525	20.0	1 : 1
	B	1.66	1.50	525	30.0	1 : 1
4	A	5.00	0.66	540	20.0	1 : 1
	B	1.66	1.50	540	30.0	1 : 1

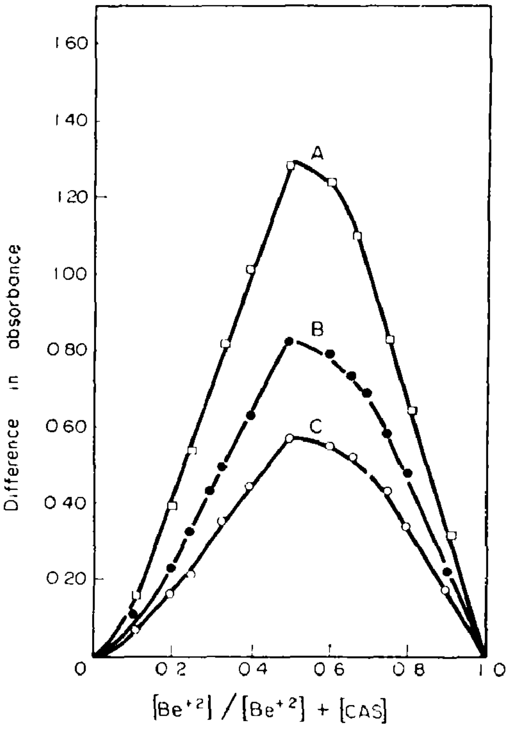


FIG. 1. Determination of composition by absorption spectra studies of equimolecular solutions at 540 mμ, pH 6.0 ± 0.2, μ 0.1 ($NaClO_4$).
Curve A, $c = 3.33 \times 10^{-4}$ M,
Curve B, $c = 2.50 \times 10^{-4}$ M,
Curve C, $c = 2.00 \times 10^{-4}$ M

TABLE 2

Method	pH	Ionic strength (M)	log K (30°C)	ΔG° at 30°C (K cals.)
Method of DEY *et al*	6.0 ± 0.2	0.1 ($NaClO_4$)	4.4 ± 0.4	6.1 ± 0.2
Mole ratio method	6.0 ± 0.2	0.1 ($NaClO_4$)	4.7 ± 0.4	6.5 ± 0.5

λ_{max} for the reagent alone shifts from 425 mμ in a neutral or slightly acidic medium to 595 mμ in a strongly alkaline medium, in which the phenolic hydrogen will be ionized **Hence** *it is likely that chelation in the present case involves the phenolic oxygen and the adjacent carboxylic oxygen and not the quinoid oxygen and the oxygen of the adjacent carboxylic group, since λ_{max} for the chelate is at 540 mμ (nearer to 590 mμ than 425 mμ) This would lead to the formation of an anionic complex,* which has been confirmed by the complete adsorption of the violet colour by the ion-exchange resin Amberlite IR-45 (OH)

Analytical applications

Experiments were performed to test the suitability of the chelate for the colorimetric determination of beryllium Beer's Law is obeyed with 0.01–0.33 p p m of beryllium in presence of excess reagent, with consistent results over a wide range of temperature between pH 4.5 and 6.5 The reaction is highly sensitive, the Sandell sensitivity being 0.00045γ/cm² and the practical sensitivity being 0.0045γ/cm² Copper, aluminium, iron uranium thorium, zirconium, palladium, borate, oxalate and citrate interfere in the determination

Acknowledgment The authors are thankful to the Council of Scientific and Industrial Research, Govt of India, for supporting the work and for the award of a research fellowship to one of them (S C S)

Chemical Laboratories
University of Allahabad
Allahabad India

S C Srivastava
A K Dey

Conversion coefficient for the Ir^{192m} transition

(*Received* 6 *June* 1962)

Because of lack of exact information concerning the conversion coefficient for the 57-keV transition in the decay of the 1.45-min isomer Ir^{192m}, it was impossible to measure by direct γ-ray counting, the cross section for its formation by neutron capture Determination by an alternate method of the yield ratio for formation of the isomeric pair Ir^{192} Ir^{192m} permits an indirect evaluation of the conversion coefficient The direct methods for determination of the internal conversion coefficient are difficult because of the high numerical value, the low energy of the X-rays emitted (*L*-X-rays, energy ~12 keV) and the short half-life of the isomer Previously reported results gave a lower limit of 1000 for the total conversion coefficient(1) and a lower limit of 870 for the *L*-subshell conversion coefficient (2) Sliv(3) and Rose(4) have predicted a value of 2080 for the *L*-conversion coefficient, and Rose(4) a value of 1250 for the M-conversion coefficient for this *E*3 transition (5)

EXPERIMENTAL

The most important step in determining the conversion coefficient by the indirect method here described is the determination of the yield ratio for the isomer pair, Ir^{192m} and Ir^{192} The yield ratio is defined as the ratio of the cross sections for formation of the two isomers by thermal neutron activation of Ir^{191} Previously reported values (0.37 and 0.84)(1, 6) are in disagreement with the rule(7) that the isomer most favoured is the one with spin closest to that of the compound nucleus In Ir^{191} capture, the spin of the compound nucleus is 3/2 ± 1/2(5) and the spins of the isomers are 1 and 4 for the upper and lower states respectively (6) Our measurements (which will be discussed fully in another paper currently in preparation) gave a value for the yield ratio of 2.0 ± 0.1 using a $4\pi\beta$-γ coincidence counting technique in a direct measurement

After determining the yield ratio, the determination of the conversion coefficient is fairly straightforward A sample of 86 per cent enriched Ir^{191} was irradiated in the reactor for an accurately-timed

---

(1) C Weber, *Z Naturf*, A9, 115 (1954)

(2) J P Mize, M E Bunker and J W Starner *Phys Rev* **96,** 444 (1954)

(3) L A Sliv and I M Band, *Coefficients of Internal Conversion of Gamma Radiation, Part* **2** *L*-shell, Published in USA as Report 58-ICC-L1 University of Illinois, Physics Dept, Urbana, Illinois (1958)

(4) M E Rose, *Internal Conversion Coefficients*, Interscience, New York (1958)

(5) D J Hughes and R B Schwartz, *Neutron Cross Sections*, USAEC Report BNL-325 (1958)

(6) G Scharff-Goldhaber and M McKeown, *Phys Rev Letters* **3,** 47 (1959)

(7) E der Mateosian and M Goldhaber, *Phys Rev* **108,** 766 (1957)

1 min period at the same position in the reactor as that used for the yield ratio determination As soon as possible after removal (usually about 1 5 min) the sample was placed in a standardized position in a γ-ray spectrometer connected to a 256-channel analyser and was counted for 10 min This period is sufficient for the decay of over 99 per cent of the 1 45-min activity originally present Another 10 min count followed and was subtracted from the first The amount of activity produced was kept sufficiently low so that there was a dead-time correction of less than 1 per cent A clear determination of the number of counts in the 57-keV γ peak was thereby possible This was converted to the absolute number of γ's emitted using corrections for efficiency,(8) peak-to-total ratio,(8) iodine X-ray escape,(9) and absorption This number multiplied by the conversion coefficient (when the value of the latter is very large) is equal to the number of Ir^{192m} nuclei present at the beginning of the count It is then possible to calculate the activity of the Ir^{192m}, as a function of the conversion coefficient, at the moment of removal from the reactor The sample was counted again 1 week later (to allow any 19 hr Ir^{191} present to decay) in order to measure the activity of the 74 5-day ground state of Ir^{192} This determination was made using the 315-keV γ peak and comparing it with an Ir^{192} sample standardized in a $4\pi/\beta$-γ coincidence counter The relationship used to calculate α, the conversion coefficient, was derived by employing the equations

$$\sigma_m = [(A_{om})/(1 - e^{-\lambda_m t})]K \qquad (1)$$

$$\sigma_T = [(A_{oT})/(\lambda_g t)]K \qquad (2)$$

where σ_m is the cross section for the formation of the 1 45-min isomer, σ_T is the total formation cross section for the Ir^{192} isomers, A_{om} and A_{oT} refers to the activity of the upper state and to the total activity (in terms of the long-lived state) at the time of removal from the reactor, λ_m and λ_g are the decay constants of the upper and lower states, t is the duration of the irradiation, and K is a constant which includes the neutron flux and the number of target atoms in the irradiated sample For σ_m/σ_g 2 0, σ_m/σ_T 0 67 A_{om} $\gamma'_0\alpha$, where γ'_0 is the rate of 57-keV γ ray emission at the time of removal from the reactor and α is the total conversion coefficient for the process Making these substitutions, dividing equation (1) by equation (2), and rearranging, one obtains

$$\alpha = [0\ 67(1 - e^{-\lambda_m t})A_{oT}]/(\gamma'_0\lambda_g t) \qquad (3)$$

RESULTS

Two determinations were made giving α 3430 and 3390 with an average value of 3400 + 300 The error quoted represents 95 per cent confidence limits and was obtained by conservatively estimating the errors associated with each term of the expression (3) given above This is in very good agreement with the value 3330 estimated from SLIV's and ROSE's tables (3 4)

B KEISCH*

Phillips Petroleum Company
Atomic Energy Division
Idaho Falls, Idaho

---

* Present address Nuclear Science and Engineering Corp, POB 10901, Pittsburgh 36 Pennsylvania

(8) R L HEATH, *Scintillation Spectrometry Gamma-Ray Spectrum Catalogue*, USAEC Report IDO-16408 (1957)

(9) P AXEL, *Escape Peak Corrections to Gamma-Ray Intensity Measurements Made with Sodium Iodide Crystals*, USAEC Report BNL-271 (1953)

Oxidations of the iodide ion in concentrated hydrochloric acid solution

(*Received* 13 *June* 1962, *in revised form* 17 *July* 1962)

THE ultimate oxidation of the iodide ion to iodine monochloride by potassium iodate in concentrated hydrochloric acid solution was shown to occur by ANDREWS(1 2) and may be represented by the half reaction

$$I^- \rightarrow I^+ + 2e \qquad (1)$$

---

(1) L W ANDREWS, *Z Anorg Chem* **36**, 76 (1903)

(2) L W ANDREWS, *J Amer Chem Soc* **25**, 756 (1903).

The method has been extended to the indirect determination of *chromates*,(1,2) *chlorates*,(1,2) and certain higher oxides.(3,4,5)

Evidence to support the two stage oxidation of the iodide ion in concentrated hydrochloric acid solution, that is $I^- \rightarrow \frac{1}{2}I_2 + e$ and $\frac{1}{2}I_2 \rightarrow I^+ + e$, is provided by the strong brown colouration of iodine observed during the titrations of potassium iodide solutions with potassium iodate, followed by the pale brown colouration of the iodine monochloride which becomes apparent as the brown colour due to iodine disappears. While many studies have been concerned with the oxidation of the iodide ion under these conditions, little attention has been given to determining at which the second stage becomes prominent. Using solvent extraction and spectroscopic techniques, the oxidation of the iodide ion in concentrated hydrochloric acid solution by potassium iodate, potassium dichromate, chromium trioxide, lead dioxide and manganese dioxide has been studied.

EXPERIMENTAL AND RESULTS

Materials

Potassium iodide, potassium iodate, potassium dichromate, chromium trioxide, lead dioxide and iodine were all of A.R. grade. Iodine monochloride and manganese dioxide were purchased from Hopkin and Williams Ltd., the latter being of their G.P.R. grade.

TABLE 1. OXIDATION OF IODIDE ION BY VARIOUS OXIDIZING AGENTS
(Showing yields of I_2 and I^+)

Potassium iodate										
*Millimoles KIO_3	0.250	0.375	0.450	0.475	0.550	0.625	0.750	1.00		
Milliequiv. I_2	1.51	2.27	2.73	2.88	2.79	2.49	1.98	0.98		
Milliequiv. I^+	-	-	-	-	0.25	0.63	1.26	2.51		
Potassium dichromate										
*Millimoles $K_2Cr_2O_7$	0.141	0.276	0.347	0.414	0.476	0.546	0.681			
Milliequiv. I_2	0.85	1.66	2.07	2.47	2.13	1.71	0.89			
Milliequiv. I^+			–	0.01	0.37	0.78	1.60			
Chromium trioxide										
*Millimoles CrO_3	0.300	0.450	0.600	0.700	0.800	0.900	1.00	1.20	1.40	
Milliequiv. I_2	0.94	1.37	1.81	2.13	2.44	2.28	1.93	1.37	0.78	
Milliequiv. I^+				-	--	0.21	0.50	1.12	1.72	
Lead dioxide										
*Millimoles PbO_2	0.410	0.625	0.830	1.04	1.25	1.46	1.66	1.87	2.08	2.50
Milliequiv. I_2	0.82	1.18	1.70	2.08	2.48	2.10	1.64	1.28	0.84	0.06
Milliequiv. I^+	-	-			–	0.38	0.78	1.23	1.65	2.45
Manganese dioxide										
*Millimoles MnO_2	0.680	0.900	1.13	1.36	1.58	1.93	2.27			
Milliequiv. I_2	1.22	1.62	2.16	2.56	2.20	1.60	1.06			
Milliequiv. I^+		--	–	—	0.28	0.88	1.48			

* Millimoles oxidizing agent added to 25 ml KI (0.0996 M).

1. *Oxidation of the iodide ion by potassium iodate, potassium dichromate, chromium trioxide, lead dioxide and manganese dioxide*

Twenty-five ml potassium iodide solution in deionized water (0.0996 M) together with 50 ml concentrated hydrochloric acid (sp. gr. 1.18) were mixed with a measured volume of potassium iodate solution (0.025 M) or a suitable weight of each oxidizing agent in a 250 ml glass stoppered flask. The contents of the flask were extracted with 8 to 10 ml portions of carbon tetrachloride until the organic layer was colourless. The combined carbon tetrachloride extracts, after addition of 25 ml hydrochloric acid (sp. gr. 1.18), were titrated with potassium iodate (0.025 M). The aqueous layers were separately titrated against potassium iodate (0.025 M).

---

(3) A. I. VOGEL, *A Textbook of Quantitative Inorganic Analysis*, 3rd Edition, p. 374, Longmans (1961).
(4) R. S. DEAN, *Chem. News* **111**, 2 (1915).
(5) G. S. JAMIESON, *Volumetric Iodate Methods*, p. 40, Chemical Catalog Co. (1926).

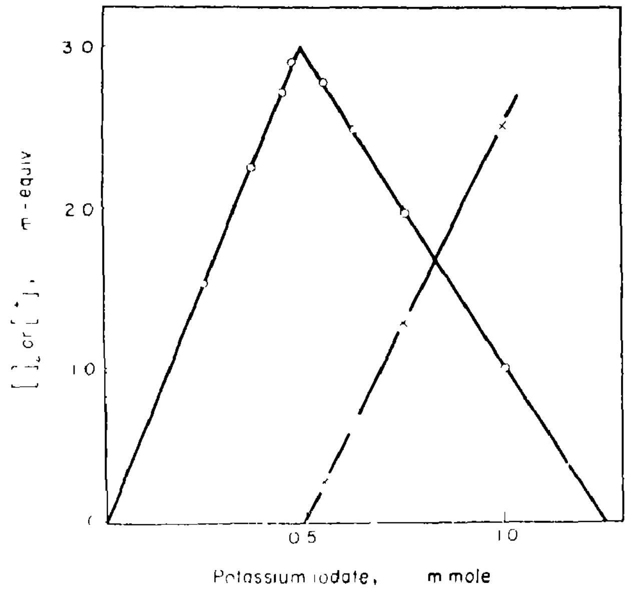


FIG. 1 Oxidation of iodide ion by potassium iodate
(○) Iodine
Iodine monochloride

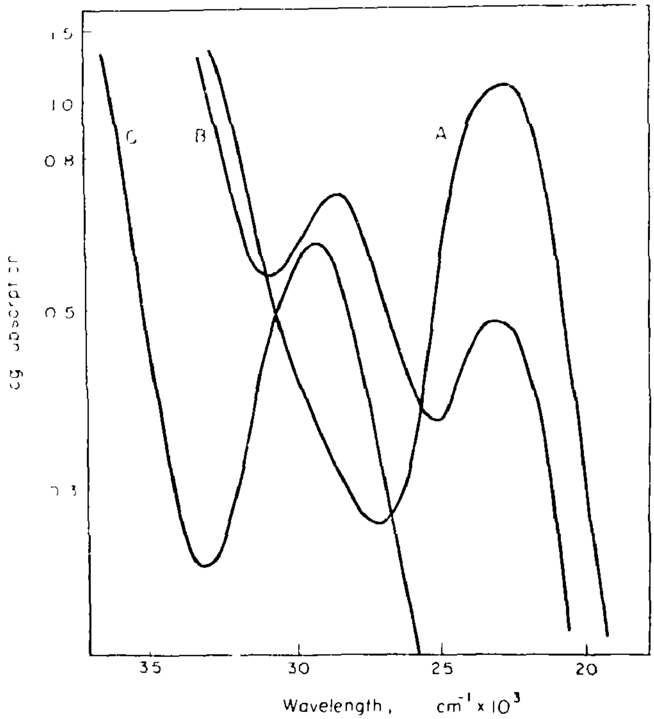


FIG. 2 Absorption spectra of iodine (A), I_3 (B) and iodine monochloride (C) in hydrochloric acid solution

For each weight of oxidizing agent selected and without solvent extraction the titration was repeated, when the volume of potassium iodate matched that required for each of the separate titration at the same weight

Table I summarizes the yields of iodine (I_2) and iodine monochloride [I(; I)] for various concentrations of oxidizing agent and Fig 1 illustrates the characteristic linear increase in iodine (I_2) concentration from zero to a maximum with a subsequent fall in its concentration coupled with an increase in the iodine [I(I)] concentration

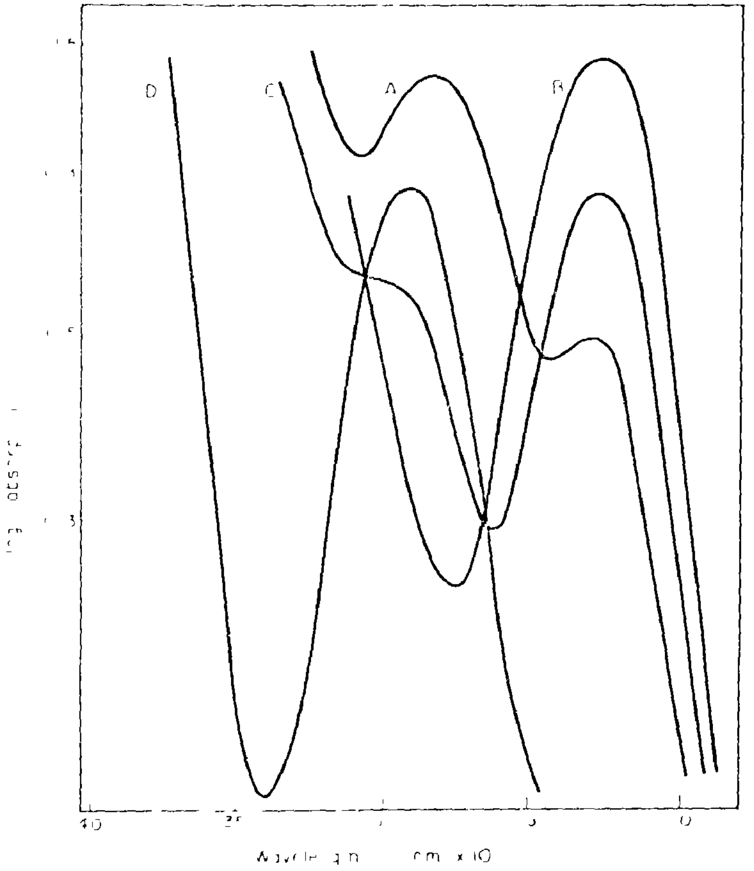


FIG 3 Absorption spectra at various points in the oxidation of iodide ion by potassium iodate
A 0 125 mM KIO_3
B 0 500 mM KIO_3
C 0 875 mM KIO_3
D 1 25 mM KIO_3

2 *Spectroscopic measurements*

All spectra were recorded between 50,000 cm $^{-1}$ and 18,000 cm $^{-1}$ using a S P 700 Unicam Recording Spectrophotometer 1 cm silica cells were used and the reference solution was a 50 65 mixture of concentrated hydrochloric acid (sp gr 1 18) and deionized water

(a) *Spectra of iodine, I_3 , and iodine monochloride* 0 03 g iodine was dissolved in 115 ml of the reference solution and an aliquot examined spectroscopically The spectrum is illustrated in Fig 2(A)

0 30 g iodine together with 25 ml potassium iodide (0 0996 M), 50 ml concentrated hydrochloric acid (sp gr 1 18) and 40 ml deionized water were made up to 230 ml with reference solution The spectrum of a ten-fold dilution with reference solution was recorded and is illustrated in Fig 2(B)

Fig 2(C) illustrates the spectrum recorded for an aliquot of a solution of 0 03 g iodine monochloride in 100 ml of the reference solution

(b) *Spectra of potassium iodide/potassium iodate mixtures* 25 ml potassium iodide (0 0996 M) and 50 ml concentrated hydrochloric acid (sp gr 1 18) were mixed with measured volumes of potassium iodate (0.025 M) and made up to 115 ml with deionized water, except that with 50 ml potassium iodate, Fig. (3D), the total volume was 125 ml. Each mixture after a ten-fold dilution with the reference solution was examined spectroscopically. The spectra are illustrated in Fig. 3.

(c) *Spectra of potassium iodide/chromium trioxide mixtures.* Known weights of chromium trioxide were reacted with 25 ml potassium iodide (0.0996 M), 50 ml concentrated hydrochloric acid (sp. gr. 1.18) and 40 ml deionized water. A ten-fold dilution of each mixture in the reference solution was spectroscopically examined and the spectra are illustrated in Fig. 4.

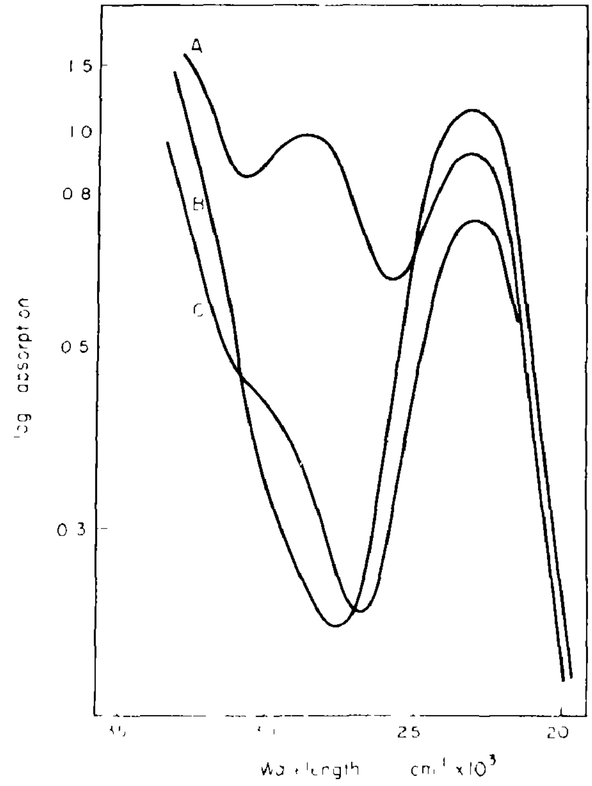


FIG. 4. Absorption spectra at various points in the oxidation of iodide ion by chromium trioxide.
A 0.600 mM CrO_3
B 0.800 mM CrO_3
C 1.20 mM CrO_3

DISCUSSION

In the overall reaction iodine can be present in at least three forms, namely, I_2, I_3^- and I^- (or its various stabilized forms). LOWRY *et al.*(6) have shown that, in aqueous solution, I_2 has a maximum in its absorption spectra at 21 500 cm^{-1} and I_3^- a maximum at 27,800 cm^{-1}. The spectra illustrated in Fig. 2 show maximum absorption for I_3^- at 28,400 cm^{-1} (curve B) and for I_2 at 22,800 cm^{-1} (curve A). These differences can be attributed to the fact that the solvent used is an aqueous solution of hydrochloric acid since shifts of this order have been observed for these species in other solvents.(7)

That the intense absorption at 29,200 cm^{-1}, Fig. (2C), also observed by GILLAM and MORTON(8) is due to the complex ICl·HCl or its anion, ICl_2^-, is supported by FAULL and BAECKSTROM(9) who maintain the cation I^+ is present in negligible concentration, or even absent, as is also suggested by FORBES, GLASS and FUOSS.(10)

---

(6) F. L. GILBERT, R. R. GOLDSTEIN and T. M. LOWRY, *J. Chem. Soc.* 1092 (1931).
(7) R. A. ZINGARO, C. A. VANDER WERF and J. KLEINBERG, *J. Amer. Chem. Soc.* **73**, 88 (1951).
(8) A. E. GILLAM and R. A. MORTON, *Proc. Roy. Soc.* A **132,** 152 (1931).
(9) J. H. FAULL and S. BAECKSTROM, *J. Amer. Chem. Soc.* **54,** 620 (1932).
(10) G. S. FORBES, S. W. GLASS and R. M. FUOSS, *J. Amer. Chem. Soc.* **47,** 2892 (1925).

The final product in the oxidation of the iodide ion has been arbitrarily represented as I^+ but this is contrary to experimental evidence.[8,9,10,11] Stabilization of I(+1) can be achieved by the formation of the ICl_2^- anion[11] thus

$$I^+ + 2Cl^- \rightarrow ICl_2^- \qquad (2)$$

During the oxidation of the iodide ion any I(+1) formed could be stabilized by unreacted iodide ion since iodine is only slightly ionized in polar solvents.[12]

$$I_2 \rightleftharpoons I^+ + I^- \qquad (3)$$

While the latter may probably occur initially, a stage is reached where the iodine yield is a maximum (Table 1, Fig. 1) and no I^- is available for this reaction to proceed further. There is, however, a considerable concentration of chloride ions available for interaction with I^+ to yield ICl_2^- (equation 2).

The steady linear increase in iodine concentration from zero to a maximum of 2.49 milliequivalents when potassium dichromate, chromium trioxide, lead dioxide and manganese dioxide are added to potassium iodide (Table 1) is consistent with the view that I^+ is unstable in the presence of the iodide ion or is not produced. In either case, the iodine can be regarded as having been produced according to the half equation $I^- - e \rightarrow \frac{1}{2}I_2$. At this maximum concentration of iodine, the iodide ions have been completely consumed as is confirmed by the absence of the I_3^- absorption in the spectrum at 28 400 cm^{-1} in the case of oxidation by chromium trioxide, (Fig. 4, curve B compared with curve A). When the oxidizing agent is present in amounts in excess of those required to consume the iodide completely, there is a steady fall in the iodine concentration coupled with an increase in the iodine (+1) concentration as shown by titration studies (Table 1) and the appearance of the characteristic ICl_2^- absorption at 29 200 cm^{-1} (Fig. 4C).

When potassium iodate is the oxidant, there is a similar linear increase in iodine concentration from zero (Table 1, Fig. 1). Spectroscopic evidence (Fig. 3) confirms the titration studies in that good resolution of molecular species at various stages in the reaction and, in particular, the additional yield of iodine produced by the reduction of the iodate (curve B), is clearly shown. The similarity of the absorption curve corresponding to complete oxidation to iodine (+1) (curve D) to that of iodine monochloride (Fig. 2C) is also noted.

CONCLUSION

The above spectroscopic, solvent extraction and volumetric studies confirm that the iodine ion, in concentrated hydrochloric acid solution, is oxidized by potassium iodate, potassium dichromate, chromium trioxide, lead dioxide and manganese dioxide in two distinct stages. The first stage corresponds to the oxidation to iodine whilst the second stage, corresponding to the oxidation of iodine to the +1 state, does not achieve prominence until the iodide has been totally consumed.

Acknowledgment—The authors thank Mr. P. F. Ellis for experimental assistance in recording the absorption spectra.

Department of Chemistry and Biology
Welsh College of Advanced Technology
Cathays Park, Cardiff

G. J. Moody
J. D. R. Thomas

[11] F. A. Philbrick, *J. Amer. Chem. Soc.* **56**, 1257 (1934).
[12] *Newer Methods of Volumetric Chemical Analysis*, Edited by W. Böttger, p. 70. Van Nostrand (1938).

The attempted preparation of AmF_6*

(*Received* 3 *July* 1962)

The hexavalent[1] and pentavalent[2] states for Am are well established, the Am is most probably present in the form of AmO_2^{++} and AmO_2^+ respectively.[3] The highest valence for the binary fluoride that has been reported is IV.[4] This was made by direct fluorination of AmF_3 up to a temperature of

---

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

[1] L. B. Asprey, S. E. Stephanou and R. A. Penneman, *J. Amer. Chem. Soc.* **72**, 1425 (1950); **73**, 5715 (1951).
[2] L. B. Werner and I. Perlman, *J. Amer. Chem. Soc.* **73**, 495 (1951).
[3] L. H. Jones and R. A. Penneman, *J. Chem. Phys.* **21**, 542 (1953).
[4] L. B. Asprey, *J. Amer. Chem. Soc.* **76**, 2019 (1954).

500 C An earlier attempt to prepare AmF_4 by fluorination of Am (III) fluoride at elevated temperatures had been unsuccessful [5] Thermal data indicates that the free energy change for the reaction, $AmF_3(c) + \frac{1}{2}F_2(g) \rightarrow AmF_4(c)$, is -22 kcal/M at 1000°K in agreement with the successful preparation of the tetrafluoride [4] Similar considerations suggested than AmF_6 could also be prepared However, when an Am (V) compound was heated in F_2 up to 500°C, $KAmF_5$ was produced [4]

Although PuF_6 is unstable with respect to PuF_4 and F_2, it has been produced by heating PuF_4 in F_2 under special conditions [6–8] It, therefore, seemed reasonable to attempt a preparation of AmF_6 in this way However, when a mixture of AmO_2 and PuF_4 were reacted with F_2, under conditions that produced PuF_6 in 90 per cent yield, the americium was left behind as the trifluoride [5] Subsequent to this failure to produce AmF_6, PtF_6, a less stable hexafluoride than PuF_6, was prepared [9] Prior to this synthesis of PtF_6, the existence of a hexavalent state for Pt had not been definitely established No hexavalent compounds of Pt were known in solution, and the only solid ones involved polyvalent elements for which there is the likelihood that the valence of Pt is less than six This preparation of the very unstable PtF_6 then stimulated this further attempt to prepare AmF_6, using the techniques that had been successful for PtF_6

As americium is available only in small quantities, and bearing in mind the radioactive hazards associated with handling the element, it was decided to work with samples containing not more than 1 mg of americium If this were quantitatively converted to hexafluoride, the amount produced would be too small to be handled without loss in the conventional apparatus used in this laboratory [6] It was, therefore decided to attempt the preparation of AmF_6 and PtF_6 simultaneously, the PtF_6 being prepared in larger quantity and serving as a carrier gas for transferring any AmF_6 formed to a container in which it could be collected and analysed For these experiments ^{241}Am, half life 458 year, was used

A brass reactor similar to that described by WEINSTOCK, MALM and WEAVER[9] was used in the first series of experiments Americium in nitric acid solution was deposited inside a platinum U-tube and the solution evaporated to dryness The tube was slowly heated to convert the nitrate to the oxide The ends of the U-tube were connected to electrically insulated terminals The reactor was immersed in liquid nitrogen and charged with pure fluorine gas The fluorination of the platinum was initiated by passing an electric current through the platinum tube When this reaction stopped, the unreacted fluorine was pumped out, the reactor was warmed, and the volatile material was condensed into a glass sampling tube Upon hydrolysis, no americium was found in the volatile product

To test the feasibility of this preparative method further, the experiment just described was repeated with the platinum tube containing a mixture of both plutonium and americium Neither of the radioactive elements was subsequently found in the volatile product except in very minute quantity and this method for the preparation of AmF_6 was then abandoned

A further attempt was made in a modified type of brass reactor in which a mixture of plutonium and americium was placed in a small nickel crucible This crucible was suspended inside of a nickel coil which was connected between the electrodes in the reactor By passing a current through the nickel coil the crucible could be heated to a bright red colour This technique was also unsuccessful for producing any conclusive evidence about the formation of a volatile americium fluoride

In the final series of experiments it was decided to try to obtain higher reaction temperatures The reactor used for this work consisted of a quartz cylinder provided with an internal quartz cold finger The mixture of americium and plutonium was placed in a shallow annular nickel trough located a few mm below the underside of the cold finger The nickel trough was heated inductively Both the cold finger and the walls of the reactor were kept at liquid nitrogen temperature during the heating of the plutonium and americium in a fluorine atmosphere A volatile product was observed to form and to condense on the walls and cold finger of the reactor This product was transferred to the sampling system and hydrolysed and analysed Radioassay showed the activity to be due entirely to plutonium Washings taken from the reactor itself accounted for all of the americium originally present

The reactor used in these final experiments was subsequently used to make the first preparation of RuF_6 and RhF_6[10, 11] These compounds had not been produced in previous attempts with a PtF_6

---

[5] S FRIED *J Amer Chem Soc* **73**, 416 (1951)

[6] B WEINSTOCK and J G MALM, *J Inorg Nucl Chem* **2**, 380 (1956)

[7] A E FLORIN, I R TANNENBAUM and J F LEMONS, *J Inorg Nucl Chem* **2**, 368 (1956)

[8] C J MANDLEBERG, H K RAE, R HURST, G LONG, D DAVIES and K E FRANCIS, *J Inorg Nucl Chem* **2**, 358 (1956)

[9] B WEINSTOCK, H H CLAASSEN and J G MALM, *J Amer Chem Soc* **79**, 5832 (1957), B WEINSTOCK, J G MALM and E E WEAVER, *J Amer Chem Soc* **83**, 4310 (1961)

[10] H H CLAASSEN, H SELIG, J G MALM, C L CHERNICK and B WEINSTOCK, *J Amer Chem Soc* **83** 2390 (1961)

[11] C L CHERNICK, H H CLAASSEN and B WEINSTOCK, *J Amer Chem Soc* **83**, 3165 (1961)

type reactor and RhF$_6$ is probably less unstable than PtF$_6$. These experiments then give further and perhaps conclusive evidence for the non-existence of AmF$_6$.

Argonne National Laboratory
Argonne, Illinois

S. Tsujimura*
D. Cohen
C. L. Chernick

Ford Motor Company
Scientific Research Laboratory
Dearborn, Michigan

B. Weinstock

---

* Present address: Japan Atomic Energy Research Institute, Tokai Laboratory, Japan

J Inorg Nucl Chem 1963 Vol 25 pp 229 to 235 Pergamon Press Ltd Printed in Northern Ireland

LETTERS TO THE EDITORS

Some pentachloro-n-alkylamino-triphosphonitriles

(*Received* 2 *August* 1962)

THE well-known aminolysis of hexachloro-triphosphonitrile ordinarily leads to the replacement of two, three, four, or six chlorine atoms (1 5) Observations that this reaction is a stepwise process and that the product is commonly controlled by the quantity of amine used suggest that all of the possible aminolysis products may be isolatable (3,6) It is of interest, however, that of the possible mono-amino derivatives, only a few obtained from simple and cyclic secondary amines,(3 6) esters of amino acids,(6) and ethyleneimine(7) have been described We have found it possible to prepare such derivatives of primary *n*-alkylamines in substantial yields by treating the hexachloro compound with the amine in a 1 2* mole ratio in an ether–water system

TABLE 1 —PROPERTIES OF SOME PENTACHLORO-*n*-ALKYLAMINO-TRIPHOSPHONITRILES

Compound	M p	B p	Yield		Analysis (%)		
	(C)	[C (mm Hg)]	(%)		C	H	N
$N_3P_3Cl_5NHCH_3$	69		10	Calc	3 50	1 18	16 37
				Found	3 63	1 21	16 74
$N_3P_3Cl_5NHCH_2CH_3$	-	105(0 05 mm)	23	Calc	6 73	1 70	15 72
				Found	6 36	1 65	15 78
$N_3P_3Cl_5NH(CH_2)_2CH_3$	--	137(1 75 mm)	53	Calc	9 72	2 18	15 12
				Found	9 79	2 31	15 30
$N_3P_3Cl_5NH(CH_2)_3CH_3$	—	110(0 05 mm)	56	Calc	12 49	2 62	14 84
				Found	12 49	2 65	14 31
$N_3P_3Cl_5NH(CH_2)_4CH_3$	—	115(0 05 mm)	37	Calc	15 07	3 04	14 06
				Found	14 81	3 00	14 28

In a typical synthesis, 50 g (0 143 mole) of hexachlorotriphosphonitrile was dissolved in 300 ml of diethyl ether and 200 ml of an aqueous solution containing 0 34 mole of the amine* was added dropwise with vigorous stirring When the reaction was complete, the ether layer was removed, dried with

* For gaseous amines, an aqueous solution of the hydrochloride was used, followed by dropwise addition of a dilute sodium hydroxide solution

[1] L F AUDRIETH, *Rec Chem Progr* **20,** 57 (1959)
[2] M BECKE-GOEHRING, K JOHN and E FLUCK, *Z Anorg Allgem Chem* **302,** 103 (1959)
[3] S K RAY and R A SHAW, *J Chem Soc* 872 (1961)
[4] R A SHAW, B W FITZSIMMONS, and B C SMITH, *Chem Revs* **62,** 247 (1962)
[5] S G KOKALIS, K JOHN, T MOELLER and L F AUDRIETH, *J Inorg Nucl Chem* **19,** 191 (1961)
[6] A A KROPACHEVA and L E MUKHINA, *Zhur Obshchei Khim* **31,** 1036 (1961)
[7] A A KROPACHEVA and L E MUKHINA, *Zhur Obshchei Khim* **31,** 2437 (1961)

calcium chloride and filtered. Evaporation of the ether left a colourless oil or solid that was purified by fractional distillation or sublimation.

Data describing the products obtained are summarized in the Table 1.

We thank the Materials Laboratory of Wright Air Development Division, Wright-Patterson Air Force Base, Ohio (Contract AF-33(616)-7918) for financial support of this research.

University of Illinois T. Moeller
Urbana, Illinois S. Lanoux

The crystal structure of some compounds of the type $LiMe^{3+}Me^{4+}O_4$ and $LiMe^{2+}Me^{5+}O_4$

(*Received* 3 *August* 1962)

IN THE course of an investigation of compounds with spinel structure we have tried to prepare a number of compounds of the type $LiMe^{a}Me^{b}O_4$. Some of these are already known, viz. $LiCoVO_4$$^{(1)}$, $LiNiVO_4$$^{(1)}$, $LiTiRhO_4$$^{(2)}$, $LiV_2O_4$$^{(3)}$, $LiMn_2O_4$$^{(4)}$, $LiGeCrO_4$$^{( )}$ and $LiGeRhO_4$$^{( )}$.

All samples were prepared by sintering an intimate mixture of the appropriate oxides (or carbonates), the atmosphere and temperature depending on the constituents. X-ray diagrams were obtained with CoK_α radiation on a "Philips" diffractometer. For compounds with spinel structure the cation distribution was calculated from the intensities of the X-ray reflections (possible error about 5%). A survey of the results is given in Table 1.

In addition to the tabulated data the following experimental facts are noteworthy.

1. In $LiZnNbO_4$ the Zn^{2+} ions may be replaced up to 80, 50 and 20 per cent by Co^{2+}, Mg^{2+} and Ni^{2+} ions respectively. The former two ions enter the tetrahedral sites, the nickel ions, however, occupy the octahedral sites.

2. The X-ray diagrams of $LiZnSbO_4$ and $LiCoSbO_4$ show the well-known spinel reflections. In addition a great number of reflections were found which could be indexed using a tetragonal unit cell having $c/a = \frac{1}{3}$ with c equal to the cell edge of the spinel unit cell. We assume at present, that these extra reflections are superstructure reflections, brought about by an order in octahedral sites between the divalent and pentavalent cations. Presumably owing to the superstructure, two of the cube edges of the spinel unit cell are tripled to get the unit cell of the ordered structure. We will try to determine the structure in the near future.

Since a more extensive study on some properties of spinels is in preparation, we finally give only two short comments on the results.

In the first place it is striking that all $LiMe^{2+}V^{5+}O_4$ compounds obtained so far have the same structure as the corresponding Me_2GeO_4 compounds (Table 2). Our failure to prepare $LiFeVO_4$ may be due to the fact that the Fe^{2+} and V^{5+} ions are probably not coexistent.

In the second place it may be remarked that the oxygen polarization energy in spinels with Li^{+} ions on the tetrahedral sites will be one of the important factors which determine the cation distribution. Since the anion in this structure is surrounded by one tetrahedral and three octahedral cations, the oxygen polarization energy will be exceptionally large if the charge of the tetrahedral ion is 1 and the average charge of the octahedral ions $3\frac{1}{2}$. J. Smit and co-workers of this laboratory$^{(10)}$ have drawn attention to this fact for 2-3 spinels (i.e. $Me^{2+}Me_2^{3+}O_4$).

Thanks are due to Mr. C. J. M. Rooymans for carrying out the high pressure experiments.

Philips Research Laboratories G. Blasse
N.V. Philips' Gloeilampenfabrieken
Eindhoven-Netherlands

(1) J. C. Bernier, P. Poix and A. Michel, *C.R. Acad. Sci., Paris* **253**, 1578 (1961).
(2) J. F. Dulac, *Bull. Soc. Franc. Miner. Crist.* **85**, 93 (1962).
(3) B. Reuter and J. Jaskowsky, *Angew. Chem.* **72**, 209 (1960).
(4) D. G. Wickham and W. J. Croft, *J. Phys. Chem. Solids*, **7**, 351 (1958).
(5) J. Dulac, *C.R. Acad. Sci., Paris* **254**, 1312 (1962).
(6) G. Blasse, *J. Inorg. Nucl. Chem.* **25**, 136 (1963).
(7) F. C. Romeijn, *Philips Res. Repts.* **8**, 321 (1953).
(8) A. Durif-Varambon, E. F. Bertaut and R. Pauthenet, *Ann. Chim.* **1**, 525 (1956).
(9) F. Dachille and R. Roy, *Amer. J. Sci.* **258**, 225 (1960).
(10) J. Smit, R. P. van Stapele and F. K. Lotgering, *J. Phys. Soc. Japan* (In Press).

TABLE 1.—SURVEY OF THE OBTAINED COMPOUNDS $LiMe^{x}Me^{y}O_4$

$LiMe^{2+}Me^{5+}O_4$			$LiMe^{3+}Me^{4+}O_4$		
Compound	Structure*	Lattice parameters (Å)	Compound	Structure*	Lattice parameters (Å)
$LiMgVO_4$	O (h.p. S)	$a = 4.80$ $b = 10.31$ $c = 6.00$ (h.p. $a = 8.27$)	$LiAlTiO_4$	S $[Al^{3+}Ti^{4+}]$	$a = 8.34$
$LiZnVO_4$(6)	P (h.p. S)	$a = 14.18$ $c = 9.49$ (h.p. $a = 8.31$)	$LiVTiO_4$	S $[V^{3+}Ti^{4+}]$	$a = 8.35$
$LiCoSbO_4$	S* $[Co^{2+}Sb^{5+}]$	$a = 8.56$	$LiCrTiO_4$	S $[Cr^{3+}Ti^{4+}]$	$a = 8.32$
$LiZnSbO_4$	S* $[Zn^{2+}Sb^{5+}]$	$a = 8.55$	$LiFeTiO_4$	S $[Li_{1/2}^{+}Fe_{1/2}^{3+}Ti^{4+}]$	$a = 8.35$
$LiZnNbO_4$(6)	S_T* $[Li^{+}Nb^{5+}]$	$a = 8.60$ $c = 8.40$	$LiRhTiO_4$	S $[Rh^{3+}Ti^{4+}]$	$a = 8.36$
			$LiAlGeO_4$	P	$a = 13.78$ $c = 9.19$

We failed to prepare

$LiFeVO_4$, $Li(Li_{1/2}Fe_{1/2})VO_4$, $LiCuVO_4$, $LiMgSbO_4$, $LiNiSbO_4$, $LiMgNbO_4$, $LiCoNbO_4$, $LiNiNbO_4$ and analogous tantalates

We failed to prepare

$LiInTiO_4$, $LiVGeO_4$, $LiFeGeO_4$, $LiInGeO_4$, $LiAlSnO_4$, $LiCrSnO_4$, $LiFeSnO_4$

* Abbreviations h.p. high pressure modification O olivine P phenacite S spinel (octahedral site cations between the brackets)
S* spinel with superstructure S_T tetragonally deformed spinel

TABLE 2.—ANALOGY BETWEEN SOME DIVALENT METAL LITHIUM VANADATES AND THE CORRESPONDING GERMANATES

Vanadates	Germanates	Structure
$LiMgVO_4$	Mg_2GeO_4(7, 8, 9)	olivine (h.p. spinel)
$LiFeVO_4$		not obtained up till now
	Fe_2GeO_4(8)	spinel
$LiCoVO_4$(1)	Co_2GeO_4(7, 8)	spinel
$LiNiVO_4$(1)	Ni_2GeO_4(7, 8)	spinel
$LiZnVO_4$(6)	Zn_2GeO_4(8)	phenacite
$LiCuVO_4$	Cu_2GeO_4	not obtained up till now
$Li(Li_{1/2}Fe_{1/2})VO_4$	$LiFeGeO_4$	

Preparation of *cis*-dinitrobis(ethylenediamine)cobalt(III) nitrite

(*Received* 13 *August* 1962)

SEVERAL preparations of salts of the $[Co(en)_2(NO_2)_2]^+$ ion have been reported in the literature. The most usual is that of WERNER(1) as modified by HOLTZCLAW *et al.*(2) beginning with potassium hexanitrocobaltate. However, this method has several disadvantages including a starting material which is difficult to prepare in high purity and to dry thoroughly, critical temperature control, and low yield (12–15 per cent). Since the compound is not only interesting in its own right, being stable and resolvable, but is also the resolving agent recently applied most successfully to the resolution of the ethylene-dinitrilotetraacetatocobaltate ion(3) a simpler synthesis is desirable. A method using *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride requires a much shorter time and is at least twice as efficient.

EXPERIMENTAL

Thirty grams of *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride(4) are dissolved with magnetic stirring in 150 ml cold H_2O. When the salt is dissolved, the solution is cooled to about 12 in an ice-salt bath and 114 g of powdered $NaNO_2$ added over 1 or 2 min while stirring fairly rapidly. The solution changes from green to red and before all the salt has been added is bright orange-brown with the suspension of the desired *cis*-salt. The mixture is cooled and stirred 30 min longer, filtered quickly, the precipitate washed once with 20–30 ml of cold water, twice with 20–30 ml portions of absolute ethanol, and twice with similar portions of ether or acetone, sucked dry on the funnel, and air-dried. The yield of the desired salt is 20 g or 61 per cent based on the starting complex. The small amount of contaminating $NaNO_2$ and NaCl are removed in converting to the nitrate(2) and the resulting compound gives no chloride test with silver nitrate.

Electrolytic analysis for cobalt gave values of 17.5 and 17.7 per cent (theory 17.6 per cent). The qualitative test for the *cis*-isomer described by HOLTZCLAW(2) confirmed that the product was the correct isomer, as did infra-red analysis. As a final check, the compound was resolved according to the method of DWYER(3) and the specific rotation of the bromide salt found to be 0.45 (reported 0.44). It was found that allowing the diastereoisomer to stand in ice water for 2 hr rather than 10 min was advisable in order to obtain the expected yield.

I. P. HARBULAK*
University of Detroit M. J. ALBINAK†

* Present address: General Electric Co., Large Lamp Division, Cleveland, Ohio.

† Present address: Owens-Illinois Glass Co., Technical Center, Toledo, Ohio.

(1) A. WERNER, *Ber.* **34**, 1706 (1901).

(2) H. F. HOLTZCLAW, D. P. SHEETZ and B. D. MCCARTY, *Inorganic Synth. IV* p. 176, McGraw-Hill, New York, 1953.

(3) F. P. DWYER and F. L. GARVAN, *Inorganic Synth. VI* p. 192, McGraw-Hill, New York, 1960.

(4) J. C. BAILAR Jr., *Inorganic Synth. II* p. 223, McGraw-Hill, New York, 1946.

The direct determination of the normal boiling point of tin(1)

(*Received* 3 *August* 1962)

IN our studies on the density of liquid metals from their melting points to their normal boiling points it was essential to know the normal boiling points of the metals. A literature search showed that the most reliable values for tin were those reported in the review literature by STULL and SINKE (2960 K)(2) and BREWER (3000 K).(3)

While determining the density of liquid tin(4) it was observed that the tin actually boiled at 760 mm Hg, about 200 below the above literature values. To check this observation 250 g of tin (99.90%

(1) This work was supported by the National Science Foundation under Grant 18829.

(2) D. R. STULL and G. C. SINKE, Thermodynamic Properties of the Elements, *Advances in Chemistry Series* 18, American Chemical Society, Washington, D.C. 1956, p. 33.

(3) L. BREWER, Paper 3, Thermodynamic and Physical Properties of the Elements, p. 31 in *The Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics* L. L. QUILL, Editor, Vol. IV-19B, National Nuclear Energy Series, New York, McGraw-Hill, 1950.

(4) A. D. KIRSHENBAUM and J. A. CAHILL, *Trans. Quart. Amer. Soc. Metall.*, **55**, 844 (1962).

purity) were refluxed in a graphite crucible and reflux condenser under argon in the carbon tube furnace. Two calibrated "pyro" optical pyrometers[a] were used in these measurements. They were sighted into a black body cavity immersed into both the boiling liquid tin and its vapour. The tin boiled at 2780 ± 20 K at 760 mm Hg. The electrical imput of the furnace (18.0 kW) was increased by 300 watts. This resulted in an increase in furnace temperature but not in the temperature of the vapour or the boiling tin, which only boiled more vigorously.

Since the observed boiling point was approximately 200° lower than the best values reported in the review literature the same pyrometers were used as a check to determine the boiling and melting points of various metals under the same conditions used for boiling tin. The results obtained are tabulated in Table 1. They are in good agreement, within the experimental error, of the best values reported in the literature except for tin.

TABLE 1. OBSERVED NORMAL BOILING AND MELTING POINTS OF VARIOUS METALS

Metal	Purity	Observed M.P. (K)	 N.B.P. (K)		Best literature value, K
Bi	99.95		1816 ± 15		1832[10]
Sb	100.0		1907 ± 10		1910[10]
Pb	99.99		2022 ± 10		2024[10]
Pt	99.99	2040 ± 10			2046.7 ± 0.2[6]
In	99.97		2285 ± 15		2273 ± 10[7]
Ag	99.99		2468 ± 15		2450[10]
Nb	99.85	2710 ± 20			2770 ± 20[8]
					2741 ± 10[9]
				ave	2755 ± 20
Cu	99.95		2811 ± 20		2855[10]
Sn	99.90		2780 ± 20		2960
					3000

STULL and SINKE calculated the boiling points of Sn by applying the Second and Third Laws of Thermodynamics to the vapour pressure data reported by BREWER and PORTER[11] and SEARCY and FREEMAN[12] in the 10^{-6} and 10^{-4} atm range. They assumed in their calculations of the boiling point of tin that the tin vapour is monatomic since HONIG[13] showed mass spectrometrically that tin vapour is about 99% monatomic while SEARCY and FREEMAN found that the molecular weight of the vapour was 91 ± 29. If this is true at a pressure of 10^{-6} to 10^{-4} atm, it is not necessarily so at a pressure of one atmosphere.

The boiling point reported by STULL and SINKE is based on a long extrapolation of BREWER and PORTER's[11] and SEARCH and FREEMAN's[12] vapour pressure data using a constant liquid heat capacity of 7.3 cal mole^{-1} deg^{-1}. If a heat capacity of 6.0 cal mole^{-1} deg^{-1} was used, STULL[?] calculated the boiling points obtained from BREWER and PORTER's and SEARCY and FREEMAN's data to be 2787 K and 2837 K respectively. Thus the discrepancy between the boiling point observed by the authors and those reported by STULL and SINKE[?] and BREWER[?] may be due to the liquid C_p value and/or the existence of complex vapour species.

It would be desirable to determine directly the normal boiling points of the homologs of tin, namely germanium and silicon, especially since HONIG[14] has shown that Ge and Si vapours contain mono-, di-, tri- and tetratomic species and the literature shows a great disagreement as to the normal boiling point of Si.[4-6] The value varies from 2625 K to 2950 K

---

[a] Checked with the tungsten ribbon lamp at 2300 and 2500 K by The Pyrometer Instrument Company, Bergenfield, N.J.

[6] W. F. ROESER, F. R. CALDWELL and H. T. WENSEL, *Bur. Stand. J. Res.* **6**, 1119 (1931).

[7] F. J. KOHLMEYER and H. SPANDAU, *Z. Anorg. Chem.* **253**, 37 (1945).

[8] A. L. RIEMAN and C. K. GRANT, *Phil. Mag.* **22**, 34 (1936).

[9] H. T. SCHOFIELD, *Inst. Metals J.* **85**, 372 (1957).

[10] D. R. STULL and G. C. SINKE, Thermodynamic Properties of the Elements in *Advances in Chemistry Series* 18, American Chemical Society, Washington, D.C., 1956 pp. 10, 12, 16, 21, 30 (B.P. calculated from best vapour pressure, heats of sublimation and vapourization data reported in the literature and should be accurate to ± 20°).

[11] L. BREWER and R. F. PORTER, *J. Chem. Phys.* **21**, 2012 (1953).

[12] A. W. SEARCY and R. D. FREEMAN, *J. Amer. Chem. Soc.* **76**, 5229 (1954).

[13] R. E. HONIG, *J. Chem. Phys.* **21**, 573 (1953).

[14] R. E. HONIG, *J. Chem. Phys.* **22**, 1610 (1954).

A D KIRSHENBAUM
J A CAHILL

Research Institute of Temple University
4150 Henry Avenue
Philadelphia 44, Pa

[4] F BAUR and R BRUNNER *Helv Chim Acta* 17 958 (1934)
[5] O RUFF and M KONSCHAK *Z Elektrochem* 32 68 (1926)
[6] D R STULL *Private communication*

Reagent dependence in sodium and strontium extraction by di(2-ethylhexyl) phosphoric acid

(*Received 27 September 1962*)

RECENT investigations here into the chemistry of strontium extraction from sodium nitrate solutions by di(2-ethylhexyl)-phosphoric acid (HX) in benzene indicate that the dependence of the extraction coefficient $E_M = (M)_o/(M)_a$ on HX concentration is direct second power when M = Na and direct third power when M = Sr if the aqueous pH (and therefore the amount of metal extracted) is low enough so that essentially all the extractant may be considered to be in the acid form This latter case is in accord with the third power reagent dependence for calcium extraction from weak HCl solutions by xylene solutions of di(2-ethylhexyl)phosphoric acid recently reported by PEPPARD *et al*[1] who conjectured that strontium should also exhibit third-power reagent dependence

As HX in non-polar diluents is known to be a dimer $(HX)_2$[2] and since hydrogen-ion dependence for the extraction of these two metals by $(HX)_2$ was also shown to be inverse first power in the case of sodium and inverse second power in the case of strontium the following reactions are suggested

$$Na^{+} + 2(HX)_2 \rightleftharpoons NaX \cdot 3HX + H^{+}$$

and

$$Sr^{2+} + 3(HX)_2 \rightleftharpoons SrX_2 \cdot 4HX + 2H^{+}$$

These reactions may be generalized as $M^{n+} + (n+2)(HX)_2 \rightleftharpoons MX_n \cdot (n+1)HX + nH^{+}$ This is essentially the same as the reaction written by PEPPARD,[1] the difference being that no special significance is given to hydrogen bonding between ligands within the complex *

PEPPARD *et al* previously explained discrepancies between [H^{+}] dependence and reagent dependence in a series of metal extractions where the indicated stoichiometry was always $M(X_2H)_n$ by proposing the single ionization of the acid dimer $(HX)_2$ viz, $(HX)_2 \rightleftharpoons HX_2^{-} + H^{+}$, followed by chelation with the metal[3] This adequately fitted the data and thus supported the view that chelation by hydrogen-bonded ligand pairs was of primary importance It appears now, however that satisfying the coordination number of the metal may be more important The earlier data are generally consistent with this view as well as with the previous view, since in most reported[3,4] cases the accepted coordination number was twice the cation valence †

---

* Bonds between active hydrogens on the un-ionized molecules and phosphoryl oxygens on those which have formed the salt probably do occur at least to some extent

† Exceptions are the cases of uranium(VI) reported by BAES, ZINGARO and COLEMAN and by DYRSSEN and KRASOVEC, and thorium(IV) reported by PEPPARD MASON and McCARTY, accepted coordination number of 8 Using the model proposed here, a coordination number of 6 is required for both uranium and thorium (counting the uranyl oxygens in the case of uranium) In the case of Cm(III) and Cf(III) reported by PEPPARD MASON and HUCHER not enough is known of the coordination chemistry of these elements to state the usual coordination number

[1] D F PEPPARD G W MASON, S McCARTY and F D JOHNSON, *J Inorg Nucl Chem*, **24,** 321 332 (1962)

[2] C F BAES, Jr, RALPH A ZINGARO and C F COLEMAN *J Phys Chem* **62,** 129 (1958)

[3] D F PEPPARD, G W MASON, W J DRISCOLL and R J SIRONEN, *J Inorg Nucl Chem*, **7,** 276–258 (1958), D F PEPPARD, G W MASON and I HUCHER, *J Inorg Nucl Chem*, **18,** 245-258 (1961)

[4] DAVID DYRSSEN *Acta Chem Scand*, **11,** 1277 78 (1957), D DYRSSEN and F KRASOVEC *Acta Chem Scand*, **13,** 561–570 (1959), C F BAES, Jr, and H T BAKER, *J Phys Chem*, **64,** 89 (1960), D F PEPPARD, G W MASON J L MAIER and W J DRISCOLL, *J Inorg Nucl Chem*, **4,** 334 (1957), D F PEPPARD, G W MASON, and S McCARTY *J Inorg Nucl Chem*, **13,** 138 150 (1960)

As noted above, this discussion is at present limited to conditions of very low loading. When the fraction of the total di(2-ethylhexyl)phosphate in the salt form becomes significant, e.g. >1 per cent, reagent dependences and state of polymerization of the reagent change markedly. These effects are being studied and will be reported in subsequent communications.

W. J. McDowell
C. F. Coleman

Oak Ridge National Laboratory
Post Office Box X
Oak Ridge, Tennessee

J. inorg. Nucl. Chem. 1963. Vol. 25. pp. 237 to 240. Pergamon Press Ltd. Printed in Northern Ireland

COMPLEXES FORMED BY THE REACTION OF ZIRCONIUM TETRACHLORIDE WITH AMIDES*

A. CLEARFIELD† and E. J. MALKIEWICH
Titanium Alloy Manufacturing Division, National Lead Company
and
Department of Chemistry, Niagara University, Niagara Falls, New York

(*Received* 23 *May* 1962, *in revised form* 27 *July* 1962)

Abstract—Co-ordination complexes of zirconium (IV) chloride with a number of amides have been prepared and their infra-red spectra examined. The amides are bonded to the zirconium atom through the carbonyl oxygen. Tertiary amides form diaddition complexes. With primary amides products containing more than 2 amide groups per zirconium were obtained. However, it is believed that the metal atom has a co-ordination number of six in these complexes, also.

THE complexes formed by the reaction of anhydrous metal halides with amides has been the subject of a number of recent studies.[1-9] The infra-red spectra of many of the complexes have been examined to determine whether the amide is bonded to the metal through oxygen or nitrogen. Co-ordination of the amide to the metal through its oxygen atom would tend to increase the single bond character of the carbonyl group and thus shift the carbonyl stretching band to lower frequencies. At the same time, the double bond character of the C—N group would be increased with consequent shifting of its stretching band to higher frequencies. In the case of metal to nitrogen bonding the frequency shifts would be just the reverse of those cited above. The majority of infra-red studies have shown metal-oxygen bonding to occur.[1,5-7,8] Earlier assignments of metal-nitrogen bonding[2,3] have been re-interpreted[7-9] to accord with metal-oxygen bonding. Crystallographic studies[10] and nuclear magnetic resonance spectra[7] have also shown that the amides are bonded to the metal atoms through the carbonyl oxygen.

We were interested in examining the reactions of zirconium (IV) halides with amides. Meutterties[9] obtained monoamide derivatives by the reaction of ZrF_4 with excess N,N,N^1,N^1-tetramethylurea and dimethyl-formamide. Infra-red spectra

---

* This paper is based in part upon the thesis submitted by EDWARD J. MALKIEWICH in partial fulfillment of the requirements for the degree of Master of Science, Niagara University, 1960.

† Address: Titanium Alloy Manufacturing Division, National Lead Company, Box C, Bridge Station, Niagara Falls, New York.

[1] R. B. PENLAND, S. MIZUSHIMA, C. CURRAN and J. V. QUAGLIANO, *J. Amer. Chem. Soc.* **79**, 1575 (1957).

[2] SR. M. MARTINETTE, S. MIZUSHIMA and J. V. QUAGLIANO, *Spectrochimica Acta*, **77** (1959).

[3] E. L. MEUTTERTIES and E. G. ROCHOW, *J. Amer. Chem. Soc.* **75**, 490 (1953).

[4] J. ARCHAMBAULT and R. RIVEST, *Canad. J. Chem.* **36**, 1461 (1958).

[5] J. ARCHAMBAULT and R. RIVEST, *Canad. J. Chem.* **38**, 1331 (1960).

[6] W. GERRARD, M. F. LAPPERT and J. W. WALLIS, *J. Chem. Soc.* 2141 (1960).

[7] W. GERRARD, M. F. LAPPERT, H. PYSZORA and J. W. WALLIS, *J. Chem. Soc.* 2144 (1960).

[8] K. W. BAGNALL, A. M. DEANE, T. L. MARKIN, P. S. ROBINSON and M. A. A. STEWART, *J. Chem. Soc.* 1611 (1961).

[9] E. L. MEUTTERTIES, *J. Amer. Chem. Soc.* **82**, 1082 (1960).

[10] M. NARDELLI, *Gazz. Chim. Ital.* **89**, 1616 (1959).

showed that the amide was bonded to the metal through oxygen. **BRAUN**(11) *reported the preparation of $ZrCl_4 \cdot 4CO(NH_2)_2$ by heating a mixture of the dry reactants. In this study we report on the complexes formed by $ZrCl_4$ with a number of amides.*

RESULTS

An excess of amide was used in each of the preparations so as to consume all of the zirconium tetrachloride in the formation of the complexes. This was done to minimize the difficulty of separating the reactants from the products since $ZrCl_4$ was found to be soluble only in solvents which reacted with the complexes whereas excess amide could be washed out with inert solvents. Under these conditions the tertiary amides always formed complexes containing 2 mols of amide per mol of $ZrCl_4$. However, with primary amides the stoichiometry of the products depended upon the ratio of reactants. This is shown in Table 1. These results are somewhat similar to those obtained with $TiCl_4$.(1)

TABLE 1. STOICHIOMETRY OF $ZrCl_4$ AMIDE ADDITION COMPOUNDS

Amides	Ratio of Reactants Amide/$ZrCl_4$	Stoichiometry of Products Amide/$ZrCl_4$
$HCONH_2$	11.0	10
$HCONH_2$	8.5	8
$HCONH_2$	4.7	4
CH_3CONH_2	6.1	4
$HCON(CH_3)_2$	6.6	2
$HCON(CH_3)_2$	4.0	2
$CH_3CON(CH_3)_2$	5.1	2

The infra-red spectra of the dimethyformamide complex and the formamide complex containing 4 molecules of amide were examined. The spectra were obtained as Nujol mulls or as KBr pellets (0.5 per cent). The comparison spectra of the pure amides were run as liquids and as Nujol mulls. Only negligible differences were observed in the positions of absorption bands in Nujol as compared to either the liquid state or the solid-KBr state. The important absorption bands and their assignments are given in Table 2. The assignments for the pure amides were taken from the work of EVANS(12), GERRARD(7) and RIVEST(5).

Examination of the carbonyl and C—N vibrational shifts for the dimethylformamide complex clearly shows that oxygen-metal bonds are present. The carbonyl band is shifted to a lower frequency and the C—N vibrations to higher frequencies in accord with the expectations for metal-oxygen bonding. The spectra of the $ZrCl_4 \cdot 4HCONH_2$ complex does not lend itself to such a straightforward interpretation. There are two absorption bands which can be assigned to the carbonyl vibrations in the complex. One is at 1724 cm^{-1} and represents a positive shift whereas the other has a frequency of 1668 cm^{-1} and represents a negative shift compared to the position of the C=O band in liquid formamide. However, there is less ambiguity connected with the C—N stretching frequency at 1314 cm^{-1}. This band is shifted to higher frequencies (1370 cm^{-1}). On this basis we conclude that oxygen to zirconium

---

(11) W. W. BRAUN, Titanium Alloy Manufacturing Division, National Lead Company, Unpublished research.

(12) J. C. EVANS, *J. Chem. Phys.* **22**, 1228 (1954).

TABLE 2. INFRA-RED SPECTRA OF $ZrCl_4$–AMIDE COMPLEXES

Band assignment	ν (cm⁻¹)		
	$HCON(CH_3)_2$	$ZrCl_4 \cdot 2HCON(CH_3)_2$	Shift
Amide I (C=O)	1681 s	1658 s	23
CH_3-deformation	1382 *m*	1367 *m*	15
C–N stretch (contiguous to carbonyl)	1255 *m*	1300 *w*	45
		1245 *w*	10
C–N stretch (contiguous to methyl)	1090 s	1135 *w*	45
Band assignment	**$HCONH_2$**	**$ZrCl_4 \cdot 4HCONH_2$**	**Shift**
Amide I (C=O) stretch	1686 s	1724 s	38
		1668 s	18
Amide II (NH_2) deformation	1611 *w*	1585 *ms*	26
C–H deformation	1397 *m*	1397 *ms*	0
C–N stretch	1314 *m*	{1370 *ms* {1314 (*sh*)	56

s = strong, *m* = medium, *w* = weak, *ms* = medium-strong, *sh* = shoulder

bonding occurs in this complex also. We attribute the appearance of the band at 1724 cm⁻¹, the shoulder at 1314 cm⁻¹ and other features of the spectra to the presence of free formamide. Thus, the co-ordination number in $ZrCl_4 \cdot 4HCONH_2$ is believed to be six, the remaining formamide molecules being held in the structure by hydrogen bonds. The hydrogen bonds must be quite weak to account for the position of the carbonyl stretching frequency at 1724 cm⁻¹.

EXPERIMENTAL

Materials. Zirconium tetrachloride was purified by the method of HORRIGAN(1) and contained the following impurities: Al 0.005, Cu 0.0002, Fe 0.0002, Mg 0.005, Si 0.03%. Acetamide was purified by recrystallization from an ethyl acetate–benzene mixture (1:3) and dried under vacuum, m.p. = 80.5°C. Reagent grade formamide, dimethyl formamide and all solvents were dried over molecular sieves and distilled under a dry nitrogen atmosphere.

Analytical. Zirconium was assayed gravimetrically as ZrO_2 by dissolving 1 g of product in 50 ml water, precipitating the hydrous oxide with ammonia and igniting at 900°C for 2 hr. Chlorine was determined by the Volhard method and nitrogen by the Kjeldahl method using a selenium catalyst.

Procedure. All reactions were run in a three-neck, 500 ml round bottom flask fitted with a mercury seal stirrer, a gas inlet tube and reflux condensor. Before each reaction the apparatus was thoroughly dried and purged with dry nitrogen. The solvent was distilled directly into the reaction flask under nitrogen and the amide dissolved in the solvent. The $ZrCl_4$ was added to a dry 25 ml Erlenmeyer flask in a dry-box. The flask was then fitted with a rubber tube and sealed with a pinch clamp. The flask was now attached to one of the necks of the reaction vessel and the $ZrCl_4$ added by removing the pinch clamp and tapping the Erlenmeyer flask. The apparatus was purged with dry nitrogen during the entire run. At the completion of the reaction, the mixture was cooled and the product filtered off and washed repeatedly with dry solvent. The products were dried in a vacuum pistol for 24–72 hr. Attempts to recrystallize the complexes were unsuccessful due to the lack of suitable solvents. The complexes softened and exhibited plastic flow a few degrees below the listed melting points.

Formamide complexes. Twenty grammes of formamide (0.445 mol) was added to 200 ml of carbon tetrachloride and the mixture agitated at room temperature. Then 9 g of $ZrCl_4$ (0.039 mol) was added and agitation at room temperature continued for 45 min. The mixture was then refluxed for 2 hr during which time a light yellow solid formed. (Found: Zr, 12.83; Cl, 20.54; N, 20.02. Calc. for $ZrCl_4 \cdot 10HCONH_2$: Zr, 13.34; Cl, 20.75; N, 20.49%.)

When the formamide: $ZrCl_4$ mole ratio was reduced to 8.5:1 and refluxing continued for 14 hr a hard yellow waxy product was obtained. (Found: Zr, 15.67; Cl, 23.88; N, 18.54. Calc. for $ZrCl_4 \cdot 8HCONH_2$: Zr, 15.38; Cl, 23.90; N, 18.89%.)

---

(1) R. V. HORRIGAN, *J. Metals*, 7, *Amer. Inst. Mech. Engrs. Trans.* 203, 1118 (1955).

On reducing the mole ratio to 4.7:1 a hard dark yellow solid was obtained after refluxing 22 hr. (Found: Zr, 22.03; Cl, 33.72; N, 13.33; C, 11.26; H, 3.47. Calc. for $ZrCl_4 \cdot 4HCONH_2$: Zr, 22.08; Cl, 34.32; N, 13.56; C, 11.61; H, 2.90%; m.p. (decomposes) 240°C.)

Dimethyl formamide complex. Twenty-seven grammes (0.370 mole) of dimethyl formamide was added to 200 ml of CCl_4 in the reaction flask. Then 13 g (0.056 mole) $ZrCl_4$ was added at room temperature with stirring. The solution immediately became cloudy. Stirring was continued for 2 hr at room temperature during which time a white precipitate formed. The mixture was then refluxed for 3 hr and the solid recovered. (Found: Zr, 23.55; Cl, 37.09; N, 7.15; C, 18.11; H, 3.65. Calc. for $ZrCl_4 \cdot 2HCON(CH_3)_2$: Zr, 24.05; Cl, 37.39; N, 7.39; C, 18.94; H, 3.70%; m.p. 206–208°C.)

Acetamide complex. Fourteen grammes (0.237 mole) of acetamide was added to 200 ml benzene and then 9 g (0.039 mole) of $ZrCl_4$ added with stirring at room temperature. The mixture was refluxed for 10 hr during which time some acetamide vaporized and collected in the reflux condensor. The product was a gummy solid which was difficult to remove from the flask and difficult to wash and dry. (Found: Zr, 18.85; Cl, 29.55; N, 11.70. Calc. for $ZrCl_4 \cdot 4CH_3CONH_2$: Zr, 19.44; Cl, 30.22; N, 11.95%; m.p. 174–176°C.)

Dimethyl acetamide complex. Twenty-five grammes (0.287 mole) of N, N-dimethylacetamide was added to 200 ml benzene and then 13 g (0.056 mole) of $ZrCl_4$ added at room temperature. The mixture was refluxed for 22 hr during which time a pale yellow solid formed. (Found: Zr, 22.52; Cl, 34.00; N, 6.62; C, 23.24; H, 4.75. Calc. for $ZrCl_4 \cdot 2CH_3CON(CH_3)_2$: Zr, 22.41; Cl, 34.85; N, 6.88; C, 23.57; H, 4.45%; m.p. 248–251°C.)

Acknowledgement—We wish to thank Mr. F. SPAGNOLA of the National Lead Research Laboratories, Brooklyn, New York for taking the infra-red spectra and Professor R. RIVEST for helpful discussions during the course of the work.

J. Inorg. Nucl. Chem. 1963, Vol. 25, pp. 241 to 245. Pergamon Press Ltd. Printed in Northern Ireland

THE HEATS OF DISSOCIATION OF THE 8-QUINOLINOL AND SUBSTITUTED 8-QUINOLINOL METAL CHELATES OF URANIUM (VI), THORIUM (IV) AND SCANDIUM (III)

G. R. Horton and W. W. Wendlandt
Department of Chemistry, Texas Technological College, Lubbock, Texas

(*Received* 20 *November* 1961; *in revised form* 27 *June* 1962)

Abstract—The heats of dissociation, ΔH, were determined for the reaction

$$M(Ox)_n \cdot HOx(s) \rightarrow M(Ox)_n(s) + HOx(g)$$

for the uranium (VI), thorium (IV), and scandium (III) complexes of 8-quinolinol (HOx) and substituted 8-quinolinols such as 2-methyl-, 5,7-dichloro-, 5,7-dibromo-, 5-iodo- and 5-iodo-7-chloro-8-quinolinol. Also the heats of sublimation, ΔH_s, were determined for the above chelating agents in the temperature range of 35° to 160°. These quantities as well as the K_p, ΔF and ΔS values were calculated from dissociation pressure data obtained by a modified Knudsen effusion-cell method. For the 8-quinolinol metal chelates the order of decreasing ΔH values was $UO_2^{2+} > Th^{4+} > Sc^{3+}$. For a given metal ion, Th^{4+}, the order of decreasing ΔH values was $HOxCl_2 > HOx > HOxICl > HOxBr > HOxI$.

THE interaction between the solvate molecule, HOx, and the metal chelate, $M(Ox)_n$, in complexes of the type $M(Ox)_n \cdot HOx$, has been the subject of a number of investigations(1–15). The metal ion, M^{n+}, is UO_2^{2+}, Th^{4+}, Sc^{3+} and PuO_2^{2+}, while HOx is 8-quinolinol and mono- and disubstituted (usually 5,7-) 8-quinolinols such as 2-methyl-, 5,7-dihalo-, 5-iodo-7-chloro- and others. There is also evidence that several of the alkaline earth ions form complexes with the stoichiometry $Sr(Ox)_2 \cdot HOx$(16) and $R[Mg(Ox)_3]$(17).

Although the solvated metal chelates have been studied by chemical methods,

---

(1) J. F. Frere, *J. Amer. Chem. Soc.* **55**, 4362 (1933).

(2) F. Hecht and W. Reich-Rohrwig, *Monatsh.* **53–54**, 596 (1929).

(3) F. Hecht and W. Ehrmann, *Z. Analyt. Chem.* **100**, 98 (1935).

(4) T. Moeller and M. V. Ramaniah, *J. Amer. Chem. Soc.* **75**, 3946 (1953); **76**, 2022, 5251, 6030 (1954).

(5) L. Pokras and P. M. Bernays, *Analyt. Chem.* **23**, 757 (1951); *J. Amer. Chem. Soc.* **73**, 7 (1951).

(6) L. Pokras, M. Kilpatrick and P. M. Bernays, *J. Amer. Chem. Soc.* **75**, 1254 (1953).

(7) W. W. Wendlandt, *Analyt. Chem.* **28**, 499 (1956).

(8) N. Eswaranarayana and Bh. S. V. Raghava Rao, *Analyt. Chim. Acta* **11**, 339 (1954).

(9) K. S. Venkateswarlu and Bh. S. V. Raghava Rao, *Analyt. Chim. Acta* **12**, 554 (1955).

(10) M. Borrell and R. Paris, *Analyt. Chim. Acta* **4**, 267 (1950).

(11) W. W. Wendlandt, *Analyt. Chim. Acta* **17**, 274 (1957).

(12) F. P. Bullwinkel and P. Noble, *J. Amer. Chem. Soc.* **80**, 2955 (1958).

(13) J. H. van Tassel and W. W. Wendlandt, *J. Amer. Chem. Soc.* **81**, 813 (1959); *ibid.* **82**, 4821 (1960).

(14) J. H. van Tassel, W. W. Wendlandt and E. Sturm, *J. Amer. Chem. Soc.* **83**, 810 (1961).

(15) W. W. Wendlandt and G. R. Horton, *J. Inorg. Nucl. Chem.* In press.

(16) D. Dyrssen, *Svensk Kem. Tidskr.* **67**, 311 (1955).

(17) F. Umland and W. Hoffman, *Analyt. Chim. Acta* **17**, 234 (1957).

ultra-violet, visible and infra-red absorption spectroscopy, heat-of-solution calorimetry, thermogravimetry and X-ray diffraction analysis, the nature of the solvate molecule-metal chelate interaction is still not very well understood. The structure of the uranium (VI) 8-quinolinol complex[12] appears to be $H[UO_2(Ox)_3]$, however, other studies[13] indicate that the scandium (III) and thorium (IV) complexes are not analogous to this structure. Since the solvated metal chelates, with the possible exception of the Sc(III) and Pu (VI) compounds, readily lose the solvate molecule when heated, as given by the equation

$$M(Ox)_n \cdot HOx(s) \rightarrow M(Ox)_n(s) + HOx(g)$$

the thermodynamic functions of this reaction can be calculated from a knowledge of the dissociation pressure of the system. To obtain the latter pressures, the Knudsen effusion-cell method was employed.[18]

EXPERIMENTAL

Reagents. 8-Quinolinol, 5,7-dibromo-8-quinolinol, and 5,7-dichloro-8-quinolinol were obtained from Eastman Organic Chemicals, Rochester, N.Y. The compounds were purified by repeated recrystallizations from acetone. 2-Methyl-8-quinolinol, 5-iodo-8-quinolinol, 5-iodo-7-chloro-8-quinolinol and 5,7-diiodo-8-quinolinol were obtained from the Aldrich Chemical Co., Milwaukee, Wis. The compounds were purified by repeated recrystallizations from ethanol. Thorium nitrate 4-hydrate was obtained from Merck and Co., Rahway, N.J., uranium nitrate 6-hydrate was obtained from Mallinckrodt Chem. Co., St. Louis, Mo., and the scandium oxide was obtained from A. D. Mackay Inc., New York, N.Y.

All of the other chemicals used were of C.p. quality.

Preparation of metal chelates. The scandium, thorium, and uranium 8-quinolinol chelates were prepared as previously described.[illegible]

The 5,7-dihalo-8-quinolinol metal chelates were prepared as previously described.[illegible]

The 2-methyl-8-quinolinol metal chelates were prepared as previously described.[19]

After preparation, the metal chelates were dried at elevated temperatures and analysed for metal content by ignition to the metal oxide in a muffle furnace. The metal oxide contents agreed to within ±0.5 per cent of that required by theory for the solvated metal chelates.

Apparatus. The apparatus employed was similar to that previously described.[20] It consisted of an Ainsworth Type RV semi-micro vacuum recording balance to which was attached a conventional glass high vacuum system, capable of a pressure of about 5×10^{-6} mm of Hg. The aluminium effusion cell was suspended from the left balance pan by means of a platinum wire. Surrounding the effusion cell was a glass tube 2.5 cm in diameter, which was attached to the vacuum system. The lower part of this tube was immersed to a depth of about 14 cm into a thermostated, stirred oil-bath, the temperature of which could be controlled to ±0.1°C. The cylindrical effusion cell was 15 mm in diameter by 25 mm in length and was sealed off at one end by a tight fitting brass screw cap containing the suspension hook. Lead washers were employed to ensure a gas tight seal of the cell. One side of the cell was machined to a thickness of about 0.12 mm and a hole drilled in the upper portion of the wall. The area of the effusion orifice was 1.00×10^{-3} cm^2 as determined with a precision travelling microscope.

The procedure for each run consisted of the following. About 400 mg of sample was placed into the effusion cell and the cell attached to the balance. The sample was then allowed to come to the temperature of the bath while at atmospheric pressure. After attaining temperature equilibrium, the system was pre-evacuated to 0.01 mm of Hg with a mechanical fore pump before being exposed to the high vacuum part of the system. In this manner, the sample chamber and balance could be evacuated to about 5×10^{-6} mm of Hg in less than 5 min. The weight-loss of the sample was recorded on a strip-chart recorder, the full scale span of which was 10.00 mg. The time of the weight-loss interval was obtained from the movement of the chart paper, which had previously been calibrated with an electric stopclock. Duplicate and in certain cases, triplicate runs were made at any one temperature.

It is estimated that from the accuracy of recording balance, bath temperature, and effusion time, the dissociation pressures have an uncertainty error of about ±5 per cent.

---

[18] M. KNUDSEN, *Ann. Physik* **29**, 179 (1909); **32**, 809 (1910).

[19] J. P. PHILLIPS, J. F. EMERY and H. P. PRICE, *Analyt. Chem.* **24**, 1033 (1952).

[20] E. VELECKIS, F. I. ROSEN and H. M. FEDER, *J. Phys. Chem.*, **65**, 2127 (1961).

RESULTS AND DISCUSSION

The vapour-pressures of the chelating agents and the dissociation pressures of the metal chelates were calculated by means of the modified Knudsen equation

$$P_{(mm)} = 17.1435\ KG/At\ \sqrt{(T/M)}$$

where K is a constant similar to the CLAUSING factor[21] and was equal to 1.026. It was not possible to calculate this constant directly, due to the uncertainty of measuring the cell wall thickness near the effusion orifice. The constant was obtained by determining the vapour-pressure of a well-known compound, naphthalene [22] which has a vapour-pressure of 0.218 mm of Hg at 35°C.

Other terms in the KNUDSEN equation are the weight-loss G, temperature of the cell, T, time of effusion, t, and molecular weight of the effusing vapour M. The vapour-pressures of the chelating agents and the solvated metal chelates ranged in magnitude from 1×10^{-4} to 2×10^{-2} mm, however, most of the values were from 1 to 9×10^{-3} mm. It was assumed in all cases that the effusion species was monomeric in the vapour state. The vapour pressures of the normal chelates, M(Ox), were too small (10^{-8} mm) to be measurable in the temperature range studied.

The constants A and B in the vapour-pressure equation

$$\log p_{(mm)} = -A\left(\frac{1}{T}\right) + B$$

for the chelating agents and the solvated metal chelates are given in Table 1 and 2 respectively.

TABLE 1. VAPOUR-PRESSURE EQUATION CONSTANTS FOR THE CHELATING AGENTS

Chelating agent	A ($\times 10^{3}$)	B
8-quinolinol (HOx)	5.69	15.49
2-methyl-8-quinolinol ($HOxCH_3$)	4.58	12.66
5,7-dichloro-8-quinolinol ($HOxCl_2$)	4.86	11.28
5-iodo-8-quinolinol (HOxI)	6.20	14.97
5,7-dibromo-8-quinolinol ($HOxBr_2$)	4.91	10.59
5-iodo-7-chloro-8-quinolinol (HOxICl)	6.85	15.55
5,7-diiodo-8-quinolinol ($HOxI_2$)	5.79	11.87

The ΔH_v, ΔF, ΔS and K_p values for the chelating agents are given in Table 3. It was necessary to obtain the vapour-pressure data over different temperature ranges i.e. 8-quinolinol and 2-methyl-8-quinolinol from 35 to 60° while the others were obtained from about 90 to 160°. This added a necessary complication in any correlation of thermodynamic functions with structural differences because of the slight change of ΔH_v with temperature. However, taking this fact into account, it can be seen that the ΔH_v values are all in the range, 21.0–31.4 kcal mole^{-1}. Likewise the ΔF values were all in the range of 4.3–11 kcal. More pronounced differences were observed in the ΔS values which ranged from 35 to 58 cal deg^{-1}. The values for ΔH_v are similar to those obtained for some of the solid organic acids such as benzoic, maleic and fumaric acids.

The ΔH, ΔF, ΔS and K_p values for the solvated metal chelates are given in Table 4. Again, a rigorous comparison of structural differences with the thermodynamic functions obtained cannot be made because of the different temperature ranges studied.

P. CLAUSING, *Ann. Physik* [5], **12**, 961 (1932).

S. I. SKLYARENKO, B. I. MARKIN and L. B. BELYAEVA, *Zh. Fiz. Khim.* **32**, 1916 (1958).

TABLE 2 DISSOCIATION PRESSURE EQUATION CONSTANTS FOR THE METAL CHELATES

Metal chelate	A (10^3)	B
$UO_2(Ox)_2$ HOx	4 7	9 27
$UO_2(OxCH_3)_2$ $HOxCH_3$	5 65	8 9
$UO_2(OxCl_2)_2$ $HOxCl_2$	5 46	10 85
$UO_2(OxI)_2$ HOxI	4 26	8 60
$UO_2(OxBr_2)_2$ $HOxBr_2$	[illegible]	11 22
$Th(Ox)_4$ HOx	4	9 98
$Th(OxCl_2)_4$ $HOxCl_2$	5 0	9 78
$Th(OxI)_4$ HOxI	[illegible]	18
$Th(OxBr_2)_4$ $HOxBr_2$	4 14	7 48
$Th(OxICl)_4$ HOxICl	4 21	7 18
$Sc(Ox)_4$ HOx	3 72	7 23
$Sc(OxCH_3)_4$ $HOxCH_3$	2 31	4 79

However except for the $Sc(OxCH_3)_4$ $HOxCH_3$ system the temperature range was from about 110 to 150

The ΔF values showed the same narrow range as did the chelating agents, namely, 7 3 13 kcal More pronounced differences were obtained for the ΔH and ΔS values,

TABLE 3 —THERMODYNAMIC FUNCTIONS FOR THE CHELATING AGENTS

Compound	ΔH, (kcal mole⁻¹)		Temp range† (°C)	ΔF (kcal)		ΔS, (cal deg⁻¹)		K_p,* (atm)		
HOx	26 0	0 2	35 55	4 5	0 1	58	2	2 3	0 1	10^{3}
$HOxCH_3$	21 0		35 60	4 3		45			3 2	10^{3}
$HOxCl_2$	22 2		90 120	7 9	0 2	38	1		2 4	10
HOxI	28 4		90 120	7 7		56	2		3 0	10^{5}
$HOxBr_2$	22 5		90 130	9 3		35	1		3 5	10^{6}
HOxICl	31 3	0 3	110 140	9 7		58	2		2 0	10^{6}
$HOxI_2$	26 5	0 2	130 160	11	0 3	42			2 9	10^{7}

* K_p, ΔF and ΔS were calculated at 373 K

† Temperature range in which ΔH, was calculated

TABLE 4 THERMODYNAMIC FUNCTIONS FOR THE METAL CHELATES

Compound	ΔH (kcal mole⁻¹)		Temp range† (°C)	ΔF (kcal)		ΔS (cal deg⁻¹)		K_p,* (atm)		
$UO_2(Ox)_2$ HOx	21 8	0 2	100-140	11	1	29	1	4 1	0 2	10^{7}
$UO_2(OxCH_3)_2$ $HOxCH_3$	16 7		110-135	11		15	0 5	2 0	0 1	10^{7}
$UO_2(OxCl_2)_2$ $HOxCl_2$	25 0		120 150	11		38	1	2 1		10^{7}
$UO_2(OxI)_2$ HOxI	22 7		125 145	13		26		2 7		10^{8}
$UO_2(OxBr_2)_2$ $HOxBr_2$	27 6		120 150	13		39		1 5	0 05	10^{8}
$Th(Ox)_4$ HOx	20 5		80 120	8 4		32		1 2		10^{5}
$Th(OxCl_2)_4$ $HOxCl_2$	23 0		120 140	12		30		8 3	0 4	10^{-8}
$Th(OxI)_4$ HOxI	16 3		110-140	12		12	0 5	1 1	0 05	10^{7}
$Th(OxBr_2)_4$ $HOxBr_2$	18 9		125-145	11		21	1	2 9	0 1	10^{7}
$Th(OxICl)_4$ HOxICl	19 4		125 150	12		20		8 1	0 4	10^{8}
$Sc(Ox)_4$ HOx	17 0		90-110	9 6		30	1	2 4	0 1	10^{6}
$Sc(OxCH_3)_4$ $HOxCH_3$	10 6	± 0 1	50 80	7 3		9	0 5	5 2	± 0 2	10^{5}

* K_p, ΔF, and ΔS were calculated at 373 K

† Temperature range in which ΔH was calculated

ranging from 10.6 to 27.6 kcal mole^{-1} and 9-38 cal deg^{-1}, respectively In the case of the $\mathrm{Sc(Ox)_3 \cdot HOx}$ system, it is not known for certain if the dissociation reaction actually takes place in a vacuum Such a desolvation reaction is known for the $\mathrm{Sc(OxCH_3)_3 \cdot HOxCH_3}$ system(13) in vacuum but not in air at atmospheric pressure Preliminary experiments on the former in vacuum gave crystals of 8-quinolinol as identified by their melting point The complete conversion to the normal chelate, $\mathrm{Sc(Ox)_3}$, was not obtained

In comparing the ΔH values for the 8-quinolinol and 2-methyl-8-quinolinol metal chelates with a given metal ion, it is seen that the latter chelating agent always gave lower ΔH values These lower values may be attributed to the steric hindrance effect of the methyl group in the 2-position such as described for the aluminium chelate (23) It was not possible to obtain consistent data for the thorium-2-methyl-8-quinolinol system This is perhaps due to the uncertainty about the composition of the solvated compound as revealed by a recent X-ray study (24)

In comparing the ΔH values for a given metal ion with the various chelating agents the order of increasing ΔH values was different for uranium and thorium For uranium the order was $\mathrm{HOxCH_3}$ HOx $\mathrm{HO_xI}$ $\mathrm{HOxCl_2}$ $\mathrm{HOxBr_2}$, while for thorium the order was HOxI $\mathrm{HOxBr_2}$ HOxICl HOx $\mathrm{HOxCl_2}$ Consistent dissociation pressure data were not obtained for the scandium 5,7-dihalo-8-quinolinol complexes due perhaps to the difficulty in preparation of these compounds in a relatively pure state

In comparing the results of this investigation with those obtained in a recent calorimetric study(13) for the reaction

$$\mathrm{M(Ox)_n \cdot HOx(s) \rightarrow M(Ox)_n(s) + HOx(s)}------\Delta H_{\mathrm{solv}}$$

it was found that the ΔH_{solv} values for the 8-quinolinol chelates were 4.2 and -5.6 kcal mole^{-1}, for the uranium and thorium chelates, respectively These values compare favourably with the calorimetric data of -4.9 and 6.5 kcal mole^{-1}, respectively The slight differences are probably due to the different temperatures at which the ΔH and ΔH_{solv} values were determined These were 100°C for ΔH and 25°C for the ΔH_{solv} values For the ΔH_{solv} of the 2-methyl-8-quinolinol uranium chelate, a value of -4.3 kcal mole^{-1} was found in this investigation compared to -2.9 kcal mole^{-1} found in the calorimetric study (14) The reason for this discrepancy is not known at the present time The heats of solvation, ΔH_{solv}, were calculated for the scandium chelates and found to be -9.0 and -15.4 kcal mole^{-1}, for the 8-quinolinol and 2-methyl-8-quinolinol chelates, respectively However, supporting calorimetric data are lacking for these systems because of the difficulty or inability to prepare the unsolvated metal chelates

It is interesting to note that the heat of dissociation for the 8-quinolinol uranium chelate, $\mathrm{UO_2(Ox)_2 \cdot HOx}$, 21.8 kcal mole^{-1}, compares favourably with that found by quantitative differential thermal analysis (25) A value of 20 ± 2 kcal mole^{-1} was found in the latter investigation

Acknowledgement —This work was supported by the U S Atomic Energy Commission through contract No AT-(40-1)-2482

H IRVING, E J BUTLER and M F RING, *J Chem Soc* 1489 (1949)
W W WENDLANDT and G R HORTON, *J Inorg Nucl Chem* In press
W W WENDLANDT and G R HORTON, *J Inorg Nucl Chem* In press

J. Inorg. Nucl. Chem. 1963, Vol. 25, pp. 247 to 252. Pergamon Press Ltd. Printed in Northern Ireland

X-RAY AND DIFFERENTIAL THERMAL ANALYSIS STUDIES ON THE 8-QUINOLINOL AND SUBSTITUTED 8-QUINOLINOL METAL CHELATES OF THORIUM (IV), URANIUM (VI) AND SCANDIUM (III)

G. R. Horton and W. W. Wendlandt
Department of Chemistry, Texas Technological College, Lubbock, Texas

(*Received* 9 *January* 1962)

Abstract—The solvated and normal 8-quinolinol and substituted 8-quinolinols chelates of scandium (III), thorium (IV) and uranium (VI) were studied by X-ray diffraction and differential thermal analysis (DTA). The unit cell dimensions for the chelates were calculated from the X-ray data using Ito's method. DTA studies showed that the solvate molecule was evolved, giving rise to endothermic peaks in the 100–300° temperature range. This peak was followed by endothermic peaks caused by the general decomposition reaction. The E_a for the desolvation of $UO_2(Ox)_2 \cdot HOx$ was 28 kcal mole^{-1} while the ΔH was 20 ± 2 kcal mole^{-1}.

Of the many metal ions which form chelates with 8-quinolinol (HOx) and substituted 8-quinolinols, only scandium (III),(1,2) thorium (IV),(2–4) uranium (VI),(3–6) uranium (IV)(7) and plutonium (VI)(8) form "solvated" metal complexes of the type $M(Ox)_n \cdot HOx$ where M is the metal or oxy-metal ion of charge n and HOx and Ox^- are the chelating agents in the free and ionic forms, respectively.

These unusual complexes have been the subject of a number of investigations. Included among these are studies on their thermal stability,(1,7,9–15) ultra-violet, visible and infra-red absorption spectra,(4,7,16–18) thermochemistry(3,13,15,19) and structure.(1,20–22)

It is the object of this investigation to further study these complexes by the techniques of differential thermal analysis (DTA) and power X-ray diffraction analysis

---

(1) L. Pokras and P. M. Bernays, *J. Amer. Chem. Soc.* **73**, 7 (1951); *Analyt. Chem.* **23**, 757 (1951).

(2) F. Hecht and W. Reich-Rohrwig, *Monatsh. Chem.* **53–54**, 596 (1929).

(3) F. J. Frere, *J. Amer. Chem. Soc.* **55**, 4362 (1933).

(4) T. Moeller and M. V. Ramaniah, *J. Amer. Chem. Soc.* **75**, 3946 (1953); **76**, 2022 (1954).

(5) T. Moeller and M. V. Ramaniah, *J. Amer. Chem. Soc.* **76**, 6030 (1954).

(6) T. Moeller and M. V. Ramaniah, *J. Amer. Chem. Soc.* **76**, 5251 (1954).

(7) W. W. Wendlandt and G. R. Horton, *J. Inorg. Nucl. Chem.* **19**, 272 (1961).

(8) B. G. Harvey, H. G. Heal, A. G. Maddock and E. L. Rowley, *J. Chem. Soc.* 1010 (1947).

(9) S. Ishimaru, *J. Chem. Soc. Japan* **53**, 566 (1932).

(10) W. W. Wendlandt, *Analyt. Chem.* **28**, 499 (1956).

(11) T. Moeller and D. H. Wilkins, *Inorganic Syntheses* (Edited by J. C. Bailar) Vol. 4, p. 101. McGraw-Hill, New York (1953).

(12) M. Borrel and R. Paris, *Analyt. Chim. Acta* **4**, 267 (1950).

(13) J. H. Van Tassel and W. W. Wendlandt, *J. Amer. Chem. Soc.* **81**, 813 (1959).

(14) W. W. Wendlandt, *Analyt. Chim. Acta* **17**, 274 (1957).

(15) C. Duval, *Inorganic Thermogravimetric Analysis* pp. 498–510. Elsevier, Amsterdam (1953).

(16) J. H. Van Tassel and W. W. Wendlandt, *J. Amer. Chem. Soc.* **82**, 4821 (1960).

(17) N. Iswaranarayana and Bh. S. V. Raghava Rao, *Analyt. Chim. Acta* **11**, 339 (1954).

(18) K. S. Venkateswarlu and Bh. S. V. Raghava Rao, *Analyt. Chim. Acta* **12**, 554 (1955).

(19) G. R. Horton and W. W. Wendlandt, *J. Inorg. Nucl. Chem.* Submitted for publication.

(20) J. H. Van Tassel, W. W. Wendlandt and E. Sturm, *J. Amer. Chem. Soc.* **83**, 810 (1961).

(21) E. P. Bullwinkel and P. Noble, *J. Amer. Chem. Soc.* **80**, 2955 (1958).

(22) W. W. Wendlandt and G. R. Horton, *J. Inorg. Nucl. Chem.* In press.

EXPERIMENTAL

X-ray apparatus. The X-ray studies were carried out on a Norelco high-low angle diffractometer, using Cu $K\alpha$ radiation. The unit cell parameters were calculated by Ito's method (23).

The densities of all of the compounds, except 8-quinolinol, were determined by a pycnometer method using cyclohexane. The density of 8-quinolinol, because of its solubility in this solvent, was calculated from the X-ray data assuming two molecules per unit cell as was found for 8-quinolinol (24).

DTA apparatus. The DTA studies were made using a Deltatherm DTA unit built by Technical Equipment Corp., Denver, Colo. Four samples were pyrolysed per run, using previously ignited alumina as the reference material. Sample sizes ranged in weight from 75 to 100 mg and were pyrolysed in an argon atmosphere. The furnace heating rate was 10 C per min.

Quantitative DTA apparatus. The quantitative DTA studies were carried out on the apparatus as previously described. The measurements were made under a helium atmosphere using sample sizes of 50–75 mg and a furnace heating rate of 10 C per min. The apparatus was calibrated with $CuSO_4 \cdot 5H_2O$ and $BaCl_2 \cdot 2H_2O$ and had a calibration constant of 0.006257 counts per cal.

TABLE I. UNIT CELL DIMENSIONS OF METAL CHELATES

Compound	a*	b	c	α	β	γ
$Th(C_9H_6NO)_4 \cdot C_9H_6NOH$	10.64	10.92	8.40	90	105 36	90
$Th(C_{10}H_8NO)_4$	9.91	9.13	7.66	88 52	92 17′	105 6
$UO_2(C_{10}H_8NO)_2 \cdot C_{10}H_9NOH$	13.83	11.45	9.34	109 5′	84 19′	107 39′
$UO_2(C_{10}H_8NO)_2$	8.91	7.70	7.36	92 4	96 37	89 15′
$UO_2(C_9H_4Br_2NO)_2 \cdot C_9H_4Br_2NOH$	15.80	6.88	12.10	90	93 37′	90
$UO_2(C_9H_4Br_2NO)_2$	13.74	10.10	7.24	105 1′	100 38′	95 46′
$UO_2(C_9H_4Cl_2NO)_2 \cdot C_9H_4Cl_2NOH$	10.13	9.94	8.90	90	121 42′	90
$UO_2(C_9H_4Cl_2NO)_2$	11.95	10.06	7.07	103 3′	105 21′	87
8-Quinolinol	7.23	6.85	6.25	92 47′	97 16′	91 31′

C_9H_6NOH is 8-quinolinol; $C_9H_4Br_2NOH$ is 5,7-dibromo-8-quinolinol

$C_{10}H_9NOH$ is 2-methyl-8-quinolinol; $C_9H_4Cl_2NOH$ is 5,7-dichloro-8-quinolinol

* Ångstrom units

The gas evolution curves were obtained on the same apparatus as described above (2). A helium gas flow rate of 120 ml per min was employed.

Chemicals. 8-Quinolinol, m.p. 74–76, was obtained from the Matheson, Coleman and Bell Co., Norwood, Ohio; 2-methyl-8-quinolinol, m.p. 72–73.5, from the Aldrich Chemical Co., Milwaukee, Wisc.; 5,7-dichloro-8-quinolinol, m.p. 173–174, and 5,7-dibromo-8-quinolinol, m.p. 196–198, from the Eastman Organic Chemicals Co., Rochester 3, N.Y.; scandium oxide, 99.8 per cent purity, from A. D. MacKay, Inc., New York, N.Y.; thorium nitrate 4-hydrate from the Lindsay Chemical Co., West Chicago, Ill.; and uranium (VI) nitrate 6-hydrate from Merck and Co., Rahway, N.J.

All of the other chemicals used were of C.p. quality.

Preparation of metal chelates. The solvated 8-quinolinol and 2-methyl-8-quinolinol chelates of scandium were prepared according to previous methods (1,26).

The 8-quinolinol, 2-methyl-8-quinolinol, and 5,7-dihalo-8-quinolinol chelates of thorium were prepared as previously described (1,5–26).

The 8-quinolinol, 2-methyl-8-quinolinol, and 5,7-dihalo-8-quinolinol chelates of uranium (VI) were prepared as previously (6–11,25).

All of the above compounds were analysed either for metal content by ignition of the complex to the metal oxide or for nitrogen content by the Dumas method.

RESULTS AND DISCUSSION

X-ray studies. The unit cell dimensions and densities of the metal chelates and 8-quinolinol are given in Table 1 and 2, respectively.

The *d* spacings for the solvated and normal thorium chelates were only in fair agreement with those previously reported (4). There were several major low-order lines which either deviated considerably or were absent from the previous work. Also, more lines were found in this investigation for these complexes and also for 8-quinolinol. The reasons for these differences are not clear. Several differences which may have caused this discrepancy are the experimental techniques, i.e. diffractometer versus powder photographs, particle size of sample, the presence of allotropic forms of the chelates and the method of preparation. The samples used in this study were probably more crystalline than those previously employed.(1)

---

(23) T. Ito, *X-ray Studies on Polymorphism*, pp. 187–288. Maruzen, Tokyo (1949).

(24) C. Gottfried, *Strukturbericht*, Vol. 4, p. 315, Edwards Bros., Ann Arbor, Mich. (1943).

(25) W. W. Wendlandt, *Analyt. Chim. Acta* **27**, 309 (1962).

(26) J. P. Phillips, J. F. Emery and H. P. Price, *Analyt. Chem.* **24**, 1033 (1952).

It has been previously reported that all of the normal chelates with 8-quinolinol were of monoclinic symmetry whereas the solvated complexes were triclinic.(20) Thus it would seem that the introduction of the solvate molecule distorts the unit cell to a system of lower symmetry. This has not been found to be true for the substituted 8-quinolinols. In the dichloro and dibromo quinolinol complexes the introduction of the solvate molecule distorts the unit cell to a system of higher symmetry, the normal chelates are triclinic whereas the solvated chelate were of monoclinic symmetry. The reason for these differences is not known at the present time. The complexes $UO_2(OxCH_3)\cdot HOxCH_3$ and $UO_2(OxCH_3)_2$, were both of triclinic symmetry with an overall elongation of all of the axes. The greatest distortion occurred, however along the *a* and *b* axes.

TABLE 2. DENSITIES OF METAL CHELATES AT 25

Compound	Particles per unit cell	Volume (Å³)	Density (g cm⁻³)	
$Th(C_9H_6NO)_4\cdot C_9H_6NOH$	0.88	940	1.484	0.003
$Th(C_{10}H_6NO)_4$	0.84	669	1.818	0.003
$UO_2(C_{10}H_8NO)_2\cdot C_{10}H_8NOH$	2.01	1332	1.870	0.003
$UO_2(C_{10}H_8NO)_2$	1.09	501	2.126	0.003
$UO_2(C_9H_4Br_2NO)_2\cdot C_9H_4Br_2NOH$	1.04	1313	1.550	0.003
$UO_2(C_9H_4Br_2NO)_2$	0.99	941	1.525	0.003
$UO_2(C_9H_4Cl_2NO)_2\cdot C_9H_4Cl_2NOH$	0.95	762	1.876	0.003
$UO_2(C_9H_4Cl_2NO)_2$	1.11	806	1.592	0.003
8-Quinolinol	2	307	1.570*	

* Calculated from X-ray data

It is of interest to note that the complexes, $Th(Ox)_4\cdot HOx$ and $Th(Ox)_4$ were both of monoclinic symmetry and thus did not fit the general pattern for the 8-quinolinol metal chelates. The normal chelate compared to the solvated metal chelate had only a slightly larger unit cell while the volumes(20) were almost identical (932 Å³ for the 4:1 and 940 Å³ for the 5:1 chelate).

DTA *studies*. The DTA curves obtained in an argon atmosphere are given in Figs. 1 and 2.

The solvated uranium (VI) 8-quinolinol complex (Fig. 1-A), gave endothermic peaks with peak maxima temperatures at 150, 300 and 450. It was first thought that the peak at 150° was due to adsorbed water but the gas evolution curve indicated that this peak was due to some sort of rearrangement reaction since no gaseous product was evolved. Similar conclusions were drawn from a thermogravimetric analysis (TGA) curve for this compound in which no weight loss was recorded up to 220. The peak 300 corresponded to the loss of the solvated molecule of 8-quinolinol and the peak at 450° was due to the loss of the remaining chelating agent and general decomposition of the complex. The normal uranium 8-quinolinol complex, $UO_2(Ox)_2$ (Fig. 1-B), gave only an endothermic peak with a peak maxima temperature at 450. This peak corresponded to the loss of the 8-quinolinol and general decomposition as was experienced in the case of $UO_2(Ox)_2 \cdot HOx$.

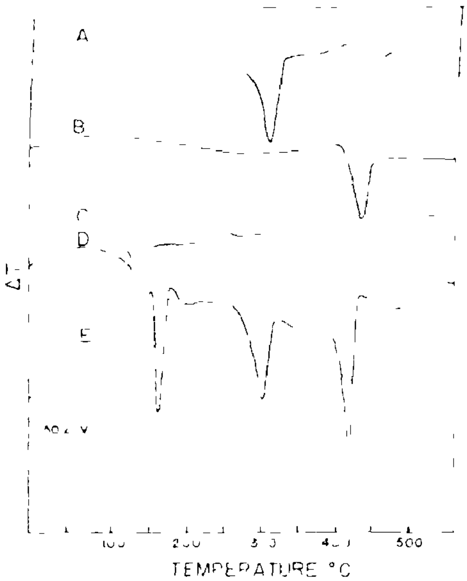


Fig. 1. Differential thermal analysis curves of 8-quinolinol complexes.
A $UO_2(Ox)_2 \cdot HOx$
B $UO_2(Ox)_2$
C $Sc(Ox)_3 \cdot HOx$
D $Th(Ox)_4 \cdot HOx$
E $Th(Ox)_4$

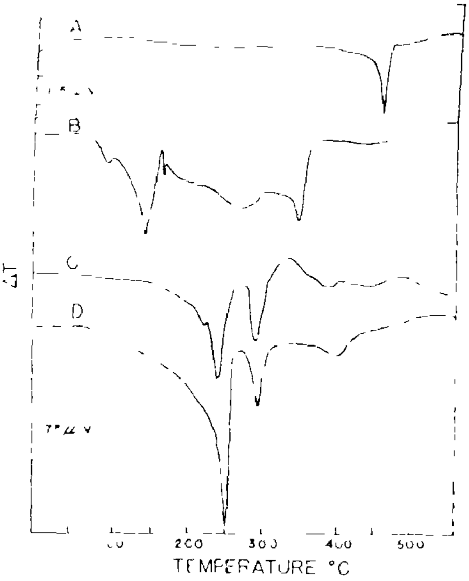


Fig. 2. Differential thermal analysis curves of 2-methyl-8-quinolinol chelates.
A $Th(OxCH_3)_4$
B $Sc(OxCH_3)_3 \cdot HOxCH_3$
C $UO_2(OxCH_3)_2$
D $UO_2(OxCH_3)_2 \cdot HOxCH_3$

The complex, $Sc(Ox)_3 \cdot HOx$ (Fig. 1-C) gave no distinct peaks which would indicate the loss of the solvated molecule of 8-quinolinol. This was in agreement with the TGA results which showed that a chelate of 3:1 stoichiometry could not be obtained by heating the 4:1 complex.[10] There was, however, a broad, ill-defined endothermic peak with a peak maximum temperature at about 120°. This peak was probably caused by the total decomposition of the complex since it is not possible to prepare the normal chelate by heating.[10]

The complex $Th(Ox)_4 \cdot HOx$ (Fig. 1-D) gave three endothermic peaks with peak maxima temperatures at 150, 310 and 410°. The peak at 150° was due to the desolvation of the complex from the 5:1 to the 4:1 chelate. This peak also contained a small endothermic shoulder peak with a peak maxima temperature at 140°. VAN TASSEL and WENDLANDT[13] have previously reported that the solvated thorium 8-quinolinol complex decomposed thermally according to a two step reaction

$$2Th(Ox)_4 \cdot HOx \rightarrow Th(Ox)_{4\,2} \cdot HOx + HOx \qquad (1)$$

$$Th(Ox)_{4\,2} \cdot HOx \rightarrow 2Th(Ox)_4 + HOx \qquad (2)$$

This could explain the occurrence of the two endothermic peaks and also the two gas evolution peaks found in the neighborhood of 150°. The remaining two peaks at 310 and 410° corresponded to the loss of the remaining 8-quinolinol and pyrolysis of the chelate. The normal complex, $Th(Ox)_4$ (Fig. 1-F), gave two endothermic peaks with peak maxima temperatures at 280 and 410°. Both of these peaks corresponded to the decomposition of the 4:1 metal chelate. The reason for the shifting of the first peak to a slightly lower temperature in the 4:1 complex is not known since both complexes gave identical peaks at 410°.

The normal 2-methyl-8-quinolinol thorium complex, $Th(OxCH_3)_4$ (Fig. 2-A), where $OxCH_3$ is the 2-methyl-8-quinolinolate ion, gave only a single endothermic peak with a peak maxima temperature at 440°. This peak was obviously caused by the general decomposition of the complex.

The solvated 2-methyl-8-quinolinol chelate, $Sc(OxCH_3)_3 \cdot HOxCH_3$ (Fig. 2-B), gave a series of endothermic peaks with peak maxima temperatures (for the prominent peaks) at 100°, 150° and 350°. The peaks at 100° and 150° probably corresponded to the desolvation reaction since it is possible to thermally convert the 4:1 to the 3:1 chelate.[16] The 3:1 chelate does not appear to be very stable as evidenced by the broad endothermic peak between 175 and 340°. The peak at 350° must also be related to this decomposition reaction.

The solvated 2-methyl-8-quinolinol uranium (VI) chelate, $UO_2(OxCH_3)_2 \cdot HOxCH_3$ (Fig. 2-D) gave two fairly large endothermic peaks with peak maxima temperatures at 250 and 300°, and a small broad peak at about 400°. When this curve is compared with that obtained for the normal chelate, $UO_2(OxCH_3)_2$ (Fig. 2-C) it is seen that the latter compound has the same peak maxima temperatures but that the 250° peak is much smaller. The only conclusion that can be drawn from this is that the desolvation reaction and decomposition of the normal chelate occur at the same time (the 250° peak) followed by further decomposition of the normal complex (the 300° peak). This behavior is different than that found for the uranium 8-quinolinol chelates.

Kinetic and heats of dissociation studies. The activation energy E_a, was determined for the desolvation reaction

$$UO_2(Ox)_2 \cdot HOx(s) \rightarrow UO_2(Ox)_2(s) + HOx(g) \tag{3}$$

by a DTA method. This method is based on the relationship

$$k = \frac{C_p \dfrac{d\Delta T}{dt} + K\Delta T}{K(A - a) - C_p\Delta T}$$

as originally derived by BORCHARDT and DANIELS[27] where k is the rate constant, K is a constant characteristic of the apparatus, A is the total peak area, C_p is the total heat capacity of the reactant or reference material, ΔT is the differential temperature, t is the time, and a is the area of the peak up to time t. Assuming first order reaction kinetics and since C_p is normally quite small, the above equation was reduced to[28, 29]

$$k = \frac{\Delta T}{A - a}$$

An Arrhenius plot of log k vs. $1/T$ resulted in a straight line whose slope yielded an

---

H. J. BORCHARDT and F. DANIELS, *J. Amer. Chem. Soc.* **79**, 41 (1957).

V. M. PADMANABHAN, S. C. SARAIYA and A. K. SUNDARAM, *J. Inorg. Nucl. Chem.* **12**, 356 (1960).

R. P. AGARWALA and M. C. NAIK, *Analyt. Chim. Acta* **24**, 128 (1960).

E_a of 28 kcal mole^{-1} for the desolvation of $UO_2(Ox)_2 \cdot HOx$. VAN [illegible] and WENDLANDT[12] have previously reported a value of 26 ± 2 kcal mole^{-1} by a thermogravimetric analysis method for the same reaction.

The heat of dissociation for $UO_2(Ox)_2 \cdot HOx$ was determined by the [illegible] of [illegible] DTA.[illegible] Using a sample size of 75 mg a value of 20 [illegible] 2 kcal [illegible] was [illegible] reaction shown in equation (3).

[illegible] U.S. Atomic Energy Commission [illegible] D. E. Sterns is gratefully ack[illegible]

[illegible] 19, 245 (1961).

J. Inorg. Nucl. Chem. 1963, Vol. 25, pp. 253 to 255. Pergamon Press Ltd. Printed in Northern Ireland

A PHASE TRANSFORMATION IN THE WURTZITE AND ZINC BLENDE LATTICE UNDER PRESSURE

C. J. M. Rooymans
Philips Research Laboratories N.V. Philips Gloeilampenfabrieken Eindhoven-Netherlands

(*Received* 2 *July* 1962)

Abstract—From the behaviour under pressure of some II–VI compounds with a wurtzite or zinc blende structure it is concluded that the high pressure polymorph of these compounds has the rock salt structure. This is confirmed by the results of a study of MnS under pressure.

An explanation for the low resistance under pressure is suggested.

In a recent article the marked effect of pressure on the absorption edge of some II–VI compounds were described.(1) We have measured the effect of pressure on the resistance at room temperature of some of these compounds, among others a CdS and a CdSe sample with wurtzite structure, in an opposed anvil apparatus.(2) The results are shown in Fig. 1. The pressures at which the resistance drops steeply are lower in our investigations than the pressures at which the large shifts in the optical absorption were found, and also lower than the pressures reported by Kafalas *et al.*(3) for the abrupt change in resistance in CdSe. It is probable that this difference is caused by a different friction in the equipment used. The effect of pressure on the resistance was reversible in these cases, with some hysteresis, as can be seen from Fig. 1.

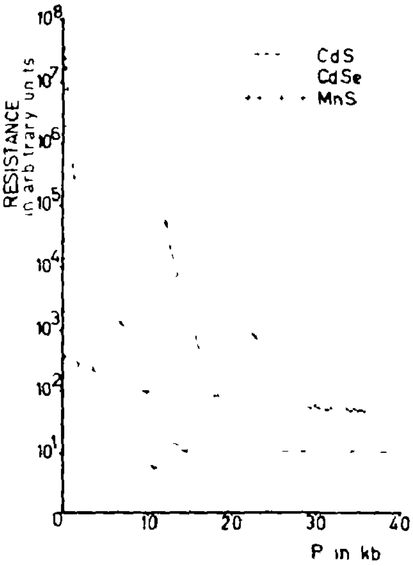


Fig. 1

As already mentioned by Edwards and Drickamer(1) for the case of CdS the X-ray diagram of such a material clearly showed a change after the pressure treatment

---

(1) A. L. Edwards and H. G. Drickamer, *Phys. Rev.* **122**, (4) 1149 (1961).
(2) D. T. Griggs and G. C. Kennedy, *Amer. J. Sci.* **254**, 722–735 (1956).
(3) J. A. Kafalas, E. P. Warekois, H. C. Gatos and M. D. Banus, Lincoln Lab., Quarterly Progress Rep. 15. 10-61, Div. 8 Group 53/26, p. 30.

The material which gave a pure wurtzite diagram before was in both cases converted for the greater part into a material which gave a zinc blende type of diagram.

Although EDWARDS et al. already mentioned the possibility of a phase transformation occurring under pressure they proposed no plausible explanation for such an event. A direct pressure-induced transition from a wurtzite to a zinc blende lattice is not to be expected as both forms have very nearly the same density. A transition to the liquid state is also not very probable from thermodynamic considerations. A transition however to a structure with six co-ordination such as the rock salt structure is quite well possible.

To check this idea a sample of MnS in the metastable wurtzite lattice was given the same pressure treatment. The dependence of the resistance on pressure was similar to the effect for CdS, the difference being that in MnS the effect was almost irreversible. After the measurements an X-ray diagram showed that the sample was completely converted into the stable rock salt type of structure.

This transition is favoured by a huge increase in density of about 20 per cent. The lattice constant of cubic MnS with rock salt structure is 5.20 Å whilst the lattice constant of metastable cubic MnS with zinc blende structure is 5.60 Å the latter being as dense as the wurtzite phase used in our experiments.

Further evidence for a transition into a rock salt type structure in these II-VI compounds is given by X-ray diagrams of CdTe samples taken after the same pressure treatment.

These diagrams of the zinc blende type phase CdTe, the resistance of which also showed a marked variation with pressure clearly exhibited extra reflexions which could be indexed for a cubic cell with a lattice constant of 5.59 Å. This indicates a Cd-Te distance (for the rock salt lattice) of 2.80 Å about the same as found in the zinc blende lattice ($\frac{1}{4}\sqrt{(3)}$ 6.43 Å). It is probable that local stresses prevented the material from returning to the original lattice, as after powdering of the thin plate-like samples, the extra reflexions had completely disappeared. The fact that this rock salt type CdTe is present under conditions of high local stresses implies that the lattice constant has a smaller value than in the case that this structure would also be stable at atmospheric pressure. This explains at the same time that the Cd-Te distance was found to be the same for both co-ordinations, which would be a deviation of the normal behaviour for ionic compounds. For comparison one must keep in mind that the Mn-S distance for nearest neighbours in the rock salt lattice is 2.60 Å, whilst this distance in the zinc blende or wurtzite type of structure is equal to 2.43 Å.

A phase transition in CdS and CdSe to the rock salt structure under pressure explains why the material after this treatment is mainly of the zinc blende type, and not of the wurtzite type of structure. When the pressure is lowered the Cd-ions return to a tetrahedral position in the neighbourhood of the formerly occupied octahedral holes without disturbing the cubic closed-packed layer structure of sulphur ions, which is the same for both the zinc blende and the rock salt structure.

It is not to be expected that a rock salt type of structure would show a much lower resistance than a zinc blende or wurtzite type of structure of the same compound. It is therefore worth mentioning that a pure MnS sample, prepared under conditions such that the rock salt structure was formed directly showed a resistance that was quite high and varied only slightly with pressure.

This is in striking contrast with the resistance of the MnS sample, transformed under pressure from the wurtzite type of lattice into the rock salt type, although it was prepared from the same raw materials.

The difference between these two samples can therefore only be the degree of ideality of the formed rock salt lattice. The drop in resistance is thus thought to be related to the great number of defects in the rock salt structure, every cation, which is not pushed from his tetrahedral place acts as an interstitial after the transformation.

It must be remarked also that the reflexions of the X-ray diagram of the pressure transformed rock salt type MnS were much broader than in the case of the directly prepared rock salt type MnS.

Preliminary measurements of the temperature coefficient of the resistance, as well as measurements of the Seebeck effect under pressure indicate a donor level at about 0.3 eV below the conduction band. This is about the same energy gap as found by SMITH and collaborators for some III-V compounds under pressure.(1)

The low resistance of the transformed phase of these compounds is therefore no justification for the assumption that the high pressure polymorph would have a structure similar to the metallic white tin structure as stated by JAYARAMAN *et al.*(2) Indium and antimony are indeed both neighbours of tin in the Periodical system, their other neighbours are however cadmium and tellurium, the compound of which has a high pressure rock salt type polymorph as stated above. A transition to a rock salt type of structure seems therefore to be as plausible for the III-V compounds as a collapse to a form similar to the white tin structure.

Note added in proof. Very recently the structure of the high pressure phase of InSb is resolved by X-ray diffraction under pressure.(3) The reflexions found were in agreement with the model proposed by JAYARAMAN *et al.*(2) namely a structure similar to white tin.

P. L. SMITH and J. E. MARTIN *Nature, Lond.* **196** (4856) 762 (1962).

Acknowledgement. I am happy to acknowledge the help of Dr. A. C. VIEN and Mr. P. C. VAN DER LINDEN of our laboratories for providing the samples and helpful discussions, and Miss J. CREEMERS for her help in the experimental work.

(1) P. L. SMITH, J. H. KING and H. A. GEBBIE, Preprints of the Symposium on the Physics and Chemistry of high Pressures 27-29 June 1962.

(2) A. JAYARAMAN, R. C. NEWTON and G. C. KENNEDY, *Nature, Lond.* **191** (4795), 1288 (1961).

(3) P. L. SMITH and J. E. MARTIN, *Nature, Lond.* **196** (4856), 762 (1962).

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 257 to 260. Pergamon Press Ltd. Printed in Northern Ireland

X-RAY STUDY AND THERMOELECTRIC PROPERTIES OF THE $NbSi_xGe_{2-x}$ AND THE $TaSi_xGe_{2-x}$ SYSTEMS

L. H. BRIXNER
E. I. du Pont de Nemours & Company
Pigments Department, Experimental Station, Wilmington, Delaware

(*Received* 18 *June* 1962)

Abstract—The AB_2-type silicides and germanides of niobium and tantalum as well as numerous solid solutions have been prepared and were structurally characterized. All compositions crystallize in the C40 type, and complete solid solubility between the corresponding silicides and germanides was experienced. The thermoelectric parameters were determined at room temperature for all compositions and also at higher temperatures for the specific composition NbSiGe.

STEELE[1] has shown that there is a rather drastic reduction of the thermal conductivity in silicon germanium alloys as compared to the individual elements. It was hoped that a similar though perhaps less spectacular reduction of thermal conductivity might be achieved with a corresponding silicide germanide system. Since the AB_2-type silicides and germanides of niobium and tantalum are isostructural and hence formation of unlimited solid solutions of the types $NbSi_xGe_{2-x}$ and $TaSi_xGe_{2-x}$ was predictable, these two systems were chosen for this investigation. The binary end members of either system are well established compounds. $NbSi_2$, $NbGe_2$ and $TaGe_2$ were first described in the literature by WALLBAUM[2,3] and $TaSi_2$ by HÖNIGSCHMID[4]. Electrical properties for $NbSi_2$ and $TaSi_2$ were reported by NESPHOR[5]. The four compositions crystallize in the C40 type of $CrSi_2$ with melting points ranging from about 1600°C to 2200°C.

EXPERIMENTAL

1. *Preparation*

The solid solutions described in this paper can be prepared either by the powder-metallurgical technique of sealing the high-purity components weighed to the nearest milligram in quartz ampoules and heating these to a reaction temperature of 1200°C for 20–30 hours or by direct combination in an arc melt. Alternatively melting can be performed by induction heating in a water-cooled copper boat. Both techniques have advantages and disadvantages. In the first case the reaction product is a powder which can easily be pressed into any desired shape but the compact needs to be sintered subsequently to develop strength. Depending on the sintering temperature, the densities obtained by this treatment varied between 80 and 95 per cent of theoretical. Arc-melted buttons as well as rods melted in the copper boat on the other hand, were essentially 100 per cent dense, but required machining in order to obtain a desired geometry. For compositions high in germanium concentration, the first route was generally preferred, the compacted bars being sintered by inductive heating in a water-cooled copper boat.

2. *Crystallographic characterization*

Samples for X-ray studies were generally taken from the centre of fused specimens. They were crushed in an agate mortar to a particle size of 325 mesh. Powder diffraction patterns were taken with a Phillips 144.6 mm diameter camera at 25°C. The samples were sealed in 0.2 mm diameter

---

M. C. STEELE and F. D. ROSI, *J. Appl. Phys.* **29**, 1517–1520 (1958).
H. J. WALLBAUM, *Z. Metallkunde* **33**, 378–381 (1941).
H. J. WALLBAUM, *Naturwissenschaften* **32**, 76–77 (1944).
O. HÖNIGSCHMID, *Monatsh. Chem.* **28**, 1017–1018 (1907).
V. S. NESPHOR and G. V. SAMSONOV, *Soviet Phys.* **5**, 877–880 (1961).

Lindemann glass capillaries and were exposed to the K_α radiation of copper (λ = 1.5418 Å) for between 4 and 6 hr. Densities were determined by vacuum-distilling CCl_4 onto the sample contained in a 5 ml pycnometer. The parameters given in Table 1 can be considered accurate to ±0.005 Å for both a_0 and c_0. If the parameters or the densities given in the table are plotted as a function of composition, a linear relationship can be observed.

TABLE 1. LATTICE PARAMETERS AND DENSITIES OF SOME SOLID SOLUTIONS OF THE $NbSi_2$–$NbGe_2$ AND $TaSi_2$–$TaGe_2$ SYSTEMS

Composition	Type	a_0 (Å)	c_0 (Å)	c/a	Number of molecules per unit cell	Unit cell volume	X-ray density (g ml⁻¹)	Pycnom density (g ml⁻¹)
$TaGe_2$	C40	4.945	6.738	1.363	3	142.575	11.392	11.28
$TaGe_{1.5}Si_{0.5}$	C40	4.910	6.706	1.366	3	140.01	10.808	10.51
$TaGe_{1.0}Si_{1.0}$	C40	4.859	6.658	1.370	3	136.135	10.300	10.24
$TaGe_{0.5}Si_{1.5}$	C40	4.840	6.635	1.371	3	134.606	9.594	9.61
$TaSi_2$	C40	4.778	6.558	1.373	3	129.657	9.104	9.06
$NbGe_2$	C40	4.943	6.778	1.371	3	142.969	8.295	8.17
$NbGe_{1.75}Si_{0.25}$	C40	4.940	6.762	1.369	3	142.905	7.911	7.79
$NbGe_{1.5}Si_{0.5}$	C40	4.910	6.730	1.371	3	140.511	7.651	7.53
$NbGe_{1.25}Si_{0.75}$	C40	4.904	6.721	1.370	3	139.976	7.261	7.21
$NbGe_{1.0}Si_{1.0}$	C40	4.885	6.682	1.368	3	138.086	6.982	6.97
$NbGe_{0.75}Si_{1.25}$	C40	4.853	6.650	1.370	3	135.631	6.701	6.43
$NbGe_{0.5}Si_{1.5}$	C40	4.834	6.635	1.373	3	134.272	6.354	6.34
$NbGe_{0.25}Si_{1.75}$	C40	4.821	6.623	1.373	3	133.305	5.986	5.90
$NbSi_2$	C40	4.803	6.604	1.375	3	131.936	5.626	5.59

3. *Electrical properties and thermal conductivity*

In order to evaluate the compositions as thermoelectric materials, the pertinent parameters were measured, namely electrical resistivity ρ (Ω cm), Seebeck coefficient S (μV/deg) and thermal conductivity κ (watts/cm deg) in order to be able to compute the "Figure of Merit" Z (deg⁻¹) given by $Z = S^2 \rho^{-1} \kappa^{-1}$. The samples used for the electrical measurements were bars ¼ in. × ¼ in. × 2 in., which were either hot-pressed (1500°C, 6000 lb/in²) or cold-pressed and subsequently sintered by inductive heating to between 1500 and 1900°C. Either procedure yielded densities around 90 per cent of theoretical and all measurements reported are characteristic of this condition only; no extrapolation to theoretical densities was attempted. The d.c. resistivities were determined by a two-point method using a standard 0.01 Ω resistance, a 2V battery as a power source and determining the potential drop with a Leeds and Northrup Type K2 potentiometer. On account of sample inhomogeneities, precision of no better than ±5 per cent can be claimed.

The Seebeck coefficient was measured with a Type K2 potentiometer in combination with a galvanometer. Thermal e.m.f. was generated by butting the bars between two copper blocks turned from the same piece of stock, one of which was heated by means of a heating tape, the other water-cooled by a coil soldered onto the block. The temperature gradient was measured by means of two thermocouples located in holes drilled to the centre of the bar immediately behind the contact faces. Here again the error will be about ±10 per cent. For the measurement of thermal conductivity, two techniques were available. One is the comparative stack technique, first described by FRANCL and KINGERY[6] which will be discussed below in connection with the high temperature data, and the other is an absolute technique similar to that described by WEISS.[7] The results in Table 2 were all obtained on samples of about 90 per cent density by the absolute technique and can probably be considered reproducible to ±10 per cent, whereas the high temperature thermal conductivity results are probably no better than ±20 per cent. The electrical properties presented in Table 2 were also measured on bars 90 per cent dense.

From the data in Table 2, it becomes apparent that the anticipated reduction of thermal conductivity by substituting germanium for silicon was achieved, although in a much less significant way than SILFIE (*loc. cit.*) experienced for the Si-Ge system. The largest difference was noticed between $NbSi_2$ and NbSiGe where κ was reduced almost by a factor of three. The fact that the thermal conductivity of $TaGe_2$ was found higher than that of $NbGe_2$ appears odd, but since the accuracy of the measurement is probably no better than ±10 per cent, the difference falls almost

---

[6] J. FRANCL and W. D. KINGERY, *J. Amer. Ceram. Soc.* **37**, 80–84 (1954).

[7] H. WEISS, *Ann. Phys. Lpz.* **4**, 121 (1959).

TABLE 2 RESISTIVITIES, SEEBECK COEFFICIENTS AND THERMAL CONDUCTIVITIES OF SOME $MeSi_xGe_{2-x}$ (Me = Nb, Ta) COMPOSITIONS

Composition	Resistivity (mΩcm) (25 °C)	Resistivity (mΩcm) (−196 °C)	Seebeck coefficient (μV/deg C)	Thermal conductivity (W/cm-deg) (25 °C)	Figure of merit Z (deg^{-1} × 10^{5}) (25 °C)
$TaGe_2$	0.035	0.013	11	0.35	0.99
$TaGe_{1.5}Si_{0.5}$	0.046	0.028	11	–	–
TaGeSi	0.060	0.033	14	0.21	1.6
$TaGe_{0.5}Si_{1.5}$	0.073	0.044	17	0.24	1.7
$TaSi_2$	0.082	0.052	18	0.37	1.1
$NbGe_2$	0.067	0.031	12	0.31	0.70
$NbGe_{1.5}Si_{0.5}$	0.077	0.063	17	0.19	2.0
NbSiGe	0.081	0.065	22	0.16	3.7
$NbSi_{1.5}Ge_{0.5}$	0.060	0.047	20	0.20	3.3
$NbSi_2$	0.038	0.063	19	0.42	0.9

within the margin of error. Note also that the reduction of κ for $TaSi_2$ by alloying with $TaGe_2$ is less pronounced than in the corresponding Nb system. The electrical properties for $NbSi_2$ and $TaSi_2$ are in fair agreement with those reported by NESPITOR (*loc. cit.*). It is apparent from these results that these silicides and germanides are substances with essentially metallic conductivity and unpromising thermoelectric properties at room temperature. Nevertheless it still appeared worthwhile to investigate the electrical behaviour of some of the compositions as a function of temperature.

The change in properties of NbSiGe represented with increasing temperature are presented in Fig. 1. An increase of the Figure of Merit from 5×10^{-5} at room temperature to 4×10^{-4} at 1000 °C was calculated from the measured parameters.

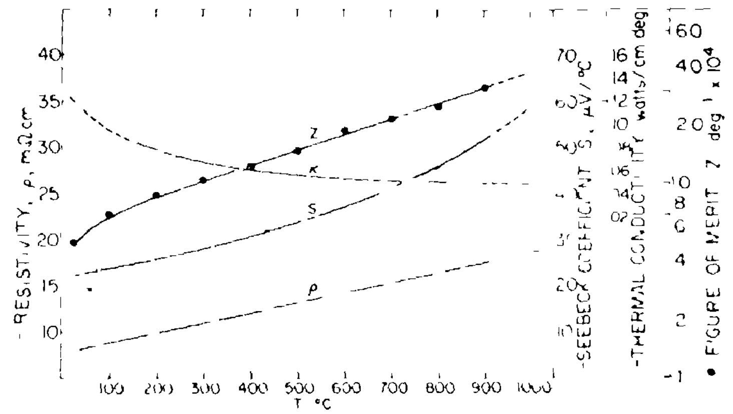


FIG. 1 Thermoelectric properties of NbSiGe as a function of temperature

The thermal conductivity of this sample was measured at elevated temperatures by the technique described by FRANCL and KINGERY (*loc. cit.*). The sample was hot-pressed into a ½ in. diameter cylinder 1 in. long. The test specimen was sandwiched between two standard alumina rods of the me dimensions, which were obtained from the Norton Company and had a reported thermal onductivity over the investigated temperature range of 0.02 w/deg-cm. The room-temperature lue of 0.12 w/cm-deg by extrapolation from the lowest point of the measurement which usually was tained at 150–180 °C is in fair agreement with the independently determined value of 0.16 w/cm-deg 30 °C. The ΔT across the sample for the high temperature measurement was kept between 10 d 20 °C. In general, the thermal conductivity decreased with increasing temperature following proximately a $T^{-1/3}$ relationship as demonstrated in Fig. 1.

The independent thermal conductivity measurement for NbSiGe was obtained on a specimen of per cent of theoretical density which had an electrical resistivity of 89 μΩcm. According to the demann–Franz Law, we can calculate the electronic contribution to the thermal conductivity to be 0.083 watts/cm-deg, which represents roughly one-half of the total conductivity. With a Seebeck coefficient of 23 μV/°C for this particular sample, a room temperature Figure of Merit of 3.7 × 10 deg^{-1} can be calculated.

Another thermal conductivity measurement was performed on a rather porous sample of only 78 per cent of theoretical density and a κ-value of 61 mW/cm-deg was observed, which is only about 38% of the value of the denser specimen. The electrical resistivity of this particular sample was 0.17 mΩ cm, a little over twice the value of the denser specimen. The Seebeck coefficient of 24 μV/°C remained approximately constant. These results suggest a shift in favour of an improved ratio between electrical and thermal conductivities upon lowering the density of the compact. This is reflected in the slightly improved Figure of Merit of 5.5 × 10, as compared to 3.7 × 10.

DISCUSSION

In summary we can state that the silicides and germanides investigated are essentially metallic in character, as deduced from the very low electrical resistivity, exhibiting a positive temperature coefficient, and the low thermoelectric power. However, since the decreasing thermal conductivity plus the increasing Seebeck coefficient more than counterbalance the rising resistivity, it appears that at high temperatures these materials may yet have a range of usefulness as power-generating thermoelectric materials, particularly since their other physical characteristics, such as high melting points, stability, and even some degree of oxidation resistance, are quite favourable as compared with, for instance, sulphides, selenides and tellurides, if indeed there is a practical need for thermoelectric energy conversion at temperatures above 1000°C.

Acknowledgement—The author greatly appreciated the assistance of Dr. G. Hetter of the Engineering Research Laboratory in obtaining the reported X-ray data.

J Inorg Nucl Chem, 1963, Vol 25, pp 261 to 270 Pergamon Press Ltd Printed in Northern Ireland

ISOTOPE EXCHANGE OF THE OXYGEN ATOMS IN MOLECULAR SIEVE ADSORBENTS WITH WATER AND CARBON DIOXIDE*

S C SAXENA† and T I TAYLOR
Chemistry Department, Columbia University, New York City, N Y

(*Received* 9 *July* 1962)

Abstract—The use of molecular sieve adsorbents for the continuous recovery of $H_2{}^{18}O$ from the gas stream of an isotope separation system is complicated by the exchange of oxygen atoms between the water and the adsorbents About 75 per cent of the oxygen atoms in the molecular sieve adsorbents exchange with $H_2{}^{18}O$ in 2 hr at 250 C At 135 C, only 24 per cent of the oxygen atoms exchange in 64 hr, and at room temperature the exchange is very slow Carbon dioxide exchanges with about the same fraction of oxygen atoms in the molecular sieve adsorbents as water does This exchange probably occurs through small quantities of water vapour since after prolonged drying under high vacuum at 250 C, the rate of exchange with carbon dioxide is somewhat slower Oxygen gas does not exchange at 250°C with molecular sieve adsorbents in the presence or absence of water-vapour

WATER-vapour is frequently removed from gas streams with calcium aluminosilicate adsorbents such as molecular sieve No 5A ‡ The method of using this adsorbent for removing and recovering $H_2{}^{18}O$ from a gas stream is influenced by the extent of oxygen isotope exchange

The reflux system for the concentration of oxygen-18 by the chemical exchange of nitric oxide with nitric acid solutions(1 2) requires the rather complete removal of water from an exit gas stream and the return of this water to the exchange column The water is produced in the final stages of the reflux system where the nitric oxide is reacted with hydrogen to form water and nitrogen Condensers, cooled to about 0°C, remove most of the $H_2{}^{18}O$ from the exit nitrogen gas stream, but this still resulted in too great a loss of enriched isotope Therefore, molecular sieve adsorbents were used to continuously recover the final traces of $H_2{}^{18}O$ from the gas stream as illustrated in Fig 1 Two adsorption tubes were placed in parallel so that one could be used while the other was regenerated After one hour of use, an automatic control system operated appropriate solenoid valves for diverting the gas flow to the second adsorption tube, admitting at the same time a back-flow of dry nitrogen for regeneration of the first tube During this regeneration, the adsorption tube was heated to about 250 C for one half hour and then allowed to cool for the remaining one half hour of the cycle

If oxygen-18 of the water exchanges with the oxygen atoms of the molecular sieve adsorbents during the above operations, the hold-up at the reflux end of the isotope exchange column will be significantly increased This will decrease the rate of increase of oxygen-18 in the exchange column Consequently, it was important to determine whether or not the molecular sieve adsorbents exchanged a significant fraction of their

---

* This research was supported in part by a grant from the U S Atomic Energy Commission, Contract AT(30-1)755

† Now at the University of Rajasthan Department of Physics Jaipur, India

‡ Product of Linde Co, Division of Union Carbide Corporation New York N Y

(1) T I TAYLOR and J C CLARKE, *J Chem Phys* **31**, 277 (1959)

(2) S C SAXENA and T I TAYLOR, *J Phys Chem* **65**, 1480 (1962)

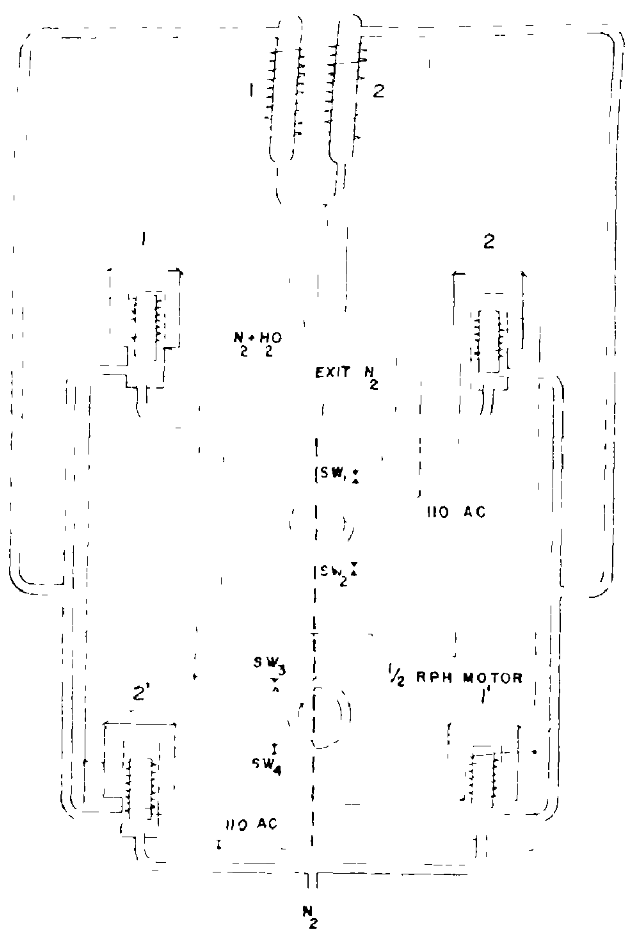


FIG. 1. Continuous recovery of $H_2^{18}O$ from a gas stream using molecular sieve adsorbents in tubes 1 and 2. The cams mounted on the shaft of a ½ rev/hr motor operate microswitches SW_1 and SW_2 to the heaters and microswitches SW_3 and SW_4 to the solenoid valves.

oxygen atoms with $H_2^{18}O$. The results should also be of interest for tracer experiments in which molecular sieve adsorbents are used as drying agents or catalysts.

EXPERIMENTAL

Adsorbents. Bulletins from the supplier* describe the general properties and composition of the molecular sieve adsorbents. JANAK *et al.*[3] have also determined a number of the properties of this adsorbent in connection with its use in gas chromotography. They report the percentage composition after drying at 450 C as: SiO_2, 40.8; Al_2O_3, 36.2; CaO, 16.0; Na_2O, 3.75; Fe_2O_3, 0.03; MgO, 0.04; K_2O, 0.05; SO_3, 0.03; loss at 950 C, 3.0 for the major components; this corresponds approximately to the mole ratio for calcium zeolite, $CaO{\cdot}Al_2O_3{\cdot}2SiO_2$. The percentage by weight of oxygen calculated from the above composition, assuming that the loss at 950 C is primarily H_2O, is 47.5 per cent.

According to the manufacturer,* the crystal structure is cubic, with a_0 = 12.32 Å (12.18 Å according to the above authors[3]) having cavities 11.4 Å in diameter connected by pores 4.2 Å in diameter. With Type 5-A molecular sieve, in which the cation is primarily calcium, the effective pore size as determined by the diameter of molecules which it will admit is 5 Å. The internal surface area is stated to be 700 to 800 m²/g of adsorbent. This area occupied by a single layer of closely packed oxygen ions of radius 1.40 Å(4) would contain from 0.24 to 0.27 g of oxygen. Since 1 g of the adsorbent contains 0.475 g of oxygen, this would correspond to a layer about two oxygen ions thick. Thus it is seen that most of the oxygen in the structures is readily accessible for exchange.

---

* Linde Co., Division of Union Carbide Corporation, New York, N.Y.

(3) J. JANAK, M. KREJCI and E. E. DUBSKY *Ann. N.Y. Acad. Sci.* **72** (13), 731 (1959).

At the partial pressures of water-vapour in our gas stream (about 5 mm of mercury), this molecular sieve adsorbs water up to 18–20 per cent of its dry mass. About 97 per cent of this water is released by regeneration with dry gas at 105 °C. Removal of the rest of the water requires temperatures up to 300 °C. Carbon dioxide is also strongly adsorbed and a small fraction remains after heating above 105 °C, probably as Na_2CO_3.(3)

Exchange experiments. Previous work(5–13) has shown that oxygen-18 in water exchanges with metal oxides, oxide catalysts, activated clays, silica, etc. at elevated temperatures. Since our use of the molecular sieve adsorbents was limited to temperatures below 250 °C, it was not possible to predict from previous work the rate or extent of the exchange. Instead of using our flow system which is more useful for high exchange rates, the exchange reactions were carried out batchwise in cylindrical glass bulbs 65 mm in diameter with volumes from 275 to 375 cm³. The bulbs were equipped with Kovar seals and metal diaphragm valves so that all parts of the bulb could be maintained at temperatures sufficiently high to prevent condensation of water-vapour. A small side tube, which was later sealed off, allowed introduction of the molecular sieve adsorbents in the form of pellets 1/8 in. in diameter. After evacuation with a mercury diffusion pump for 24–48 hr at 250 °C, the weight of the dry adsorbent (3.5–4.5 g) was determined. Water (0.20 ml, 11.1 mmole) containing 1.50 atom per cent oxygen-18 was then transferred to the reaction bulb immersed in a dry-ice bath.

Two different methods were used to follow the extent of the oxygen-18 exchange with time at several temperatures. The first one involved removing the water after a given length of time and determining the oxygen-18 content by equilibration with carbon dioxide. Since carbon dioxide equilibrates rapidly at 250 °C in the presence of the molecular sieves, it was found more convenient to add a small quantity (15–50 cm³ atmospheres) of carbon dioxide to the reaction bulb along with the water. This latter procedure allowed the removal of several samples of carbon dioxide for mass spectrometric analysis during the course of the exchange reaction. A summary of the exchange data for typical experiments is given in Tables 1 and 2.

Determination of enrichment in carbon dioxide. When samples of carbon dioxide from the reaction mixture are analysed with the mass spectrometer, one obtains the ratio R_e of the positive ion current for mass 44 to that for mass 46. The atom fraction of oxygen-18 in the CO_2 is $1/(2R_e + 1)$. However, owing to small changes with time in the discrimination by the instrument, one usually obtains the ratio R_r for a standard reference sample each time a group of samples is analysed. The reference standard is usually tank carbon dioxide or carbon dioxide from dry-ice, but preferably carbon dioxide equilibrated with water. Apparently both tank carbon dioxide and dry-ice are equilibrated with water in their manufacture and therefore the atom fraction of oxygen-18 in CO_2 from all three sources is very nearly the same and slightly enriched in oxygen-18 relative to water.

The enrichment I of oxygen-18 in the equilibrated samples of carbon dioxide relative to that in the reference standard is given by

$$I = \frac{n_e(1 - n_r)}{n_r(1 - n_e)} = \frac{1/(2R_e + 1)}{1 - 1/(2R_e + 1)} \Big/ \frac{1/(2R_r + 1)}{1 - 1/(2R_r + 1)} = \frac{R_r}{R_e} \tag{1}$$

where n_e and n_r are the atom fractions of oxygen-18 in the equilibrated and the reference carbon dioxide respectively. From equation (1) it follows that

$$n_e = \frac{I n_r}{1 + n_r(I - 1)} \tag{2}$$

L. Pauling, *The Nature of the Chemical Bond*, Cornell, Ithaca, New York (1960).

N. Marha, T. Titani and co-workers reviewed by K. H. Geib in *Handbuch der Katalyse*, p. 86–92 (Edited by G. M. Schwab) Springer Verlag, Vienna (1943).

G. A. Mills and S. G. Hindin, *J. Amer. Chem. Soc.* **72**, 5549 (1950).

E. Whalley and E. R. S. Winter, *J. Chem. Soc.* 1175 (1950).

S. M. Karpacheva and A. M. Rozen, *Dokl. Akad. Nauk U.S.S.R.* **75**, 55, 239 (1950).

A. G. Oblad, S. G. Hindin and G. A. Mills, *J. Amer. Chem. Soc.* **75**, 4096 (1953).

W. C. Cameron, A. Farkas and L. M. Litz, *J. Phys. Chem.* **57**, 229 (1953).

S. E. Weller and S. E. Voltz, *J. Amer. Chem. Soc.* **76**, 469 (1954).

Yoneda, A. Fujimoto and S. Makishima, *J. Phys. Chem.* **63**, 1987 (1959).

G. Spitzer and J. R. Ligenza, *Phys. Chem. Solids* **17**, 196 (1961).

TABLE 1 – RESULTS OF TYPICAL EXPERIMENTS ON THE EXCHANGE OF OXYGEN-18 BETWEEN WATER AND MOLECULAR ADSORBENTS. THE VALUES IN PARENTHESES ARE THE ENRICHMENTS THE CO_2 WOULD HAVE IF IT WERE EQUILIBRATED WITH WATER ALONE AT THE TEMPERATURE OF THE REACTION. MOLECULAR SIEVE ADSORBENTS ARE REPRESENTED BY MS AND BY MS-^{18}O WHEN ENRICHED IN OXYGEN-18

Run	Reactants	t (°C)	MS (g)	mmole $H_2^{18}O$ 1.50%	mmole CO_2	Time (hr)	r	%O of MS exchanged
1	(a) $H_2^{18}O$ + MS	250	3.81	11.1		2		73.7
	CO_2 + Sep. $H_2^{18}O$	25		11.1	0.62	20	1.68	
	(b) CO_2 + MS-^{18}O	250	3.81		0.62	1.2	1.68	73.7
						2.2	1.67	
2	$H_2^{18}O$ + CO_2 + MS	250	3.76	11.1	1.86	0	(5.61)	0
						0.5	1.97	49.7
						1.0	1.69	75.0
						4.0	1.67	77.7
						24.0	1.64	81.9
3	$H_2^{18}O$ + CO_2 + MS	150	3.93	11.1	1.86	0	(5.61)	0
						70	2.26	33.9
						145	2.14	38.8
4	$H_2^{18}O$ + CO_2 + MS	135	3.73	11.1	0.93	0	(6.28)	0
						1.25	4.58	7.4
						4.0	3.65	11.9
						64.3	2.70	24.0
5	$H_2^{18}O$ + CO_2	25		11.1	0.62	96	6.77	

TABLE 2 – EXCHANGE OF CO_2 AND O_2 WITH MOLECULAR SIEVE ADSORBENTS ENRICHED IN OXYGEN-18. THE VALUES IN PARENTHESES ARE THE VALUES OF r EXPECTED FOR COMPLETE EQUILIBRIUM OF CO_2 OR O_2 WITH THE READILY EXCHANGEABLE OXYGEN OF THE ADSORBENTS. THE READILY EXCHANGEABLE OXYGEN IS TAKEN AS THAT WHICH EXCHANGES WITH WATER AT 250 °C IN ABOUT 2 HR, I.E. 75 PER CENT

Run	Reactants	t (°C)	MS (g)	mmole CO_2 or O_2	Time (hr)	r	% of equil
6	CO_2 + MS-^{18}O	250	3.76	0.62	0	1.00	
					1.25	1.49	77
					2.33	1.49	77
						(1.64)	
7	CO_2 + MS-^{18}O	255	4.20	0.62	0	1.00	
					4.5	1.61	82
						(1.75)	
8	CO_2 + MS-^{18}O	26	4.20	9.5	0	1.00	
					120	1.00	0.0
						(1.74)	
9	CO_2 + MS-^{18}O	80	4.20	13.0	0	1.00	
					96	1.04	5.5
						(1.73)	
10	O_2 + MS-^{18}O	250	3.68	1.3	0	1.00	
					5	1.02	
					9.5	0.99	
						(1.72)	
11	O_2 + $H_2^{18}O$ + MS-^{18}O	250	3.68	2.1	0	1.00	
					21.0	1.03	
					46.5	1.02	
						(2.3)	

When the reference carbon dioxide is equilibrated with a large quantity of water at 25°C, oxygen-18 concentrates in the carbon dioxide with an enrichment factor, α_1, given by

$$\alpha_1 = \frac{n_r/(1 - n_r)}{N_u/(1 - N_u)} \tag{3}$$

so that

$$n_r = \frac{N_u\alpha_1}{1 + N_u(\alpha_1 - 1)} \approx N_u\alpha_1 \tag{3a}$$

where N_u is the atom fraction of oxygen-18 in the water. Since $N_u(\alpha_1 - 1)$ is very small compared to 1, the atom fraction n_r of oxygen-18 in the reference carbon dioxide is, with sufficient accuracy, given by $N_u\alpha_1$. The normal atom fraction of oxygen-18 in fresh water is 0.00204[14] and α_1 for 25°C is 1.038[15, 16] so that the atom fraction of oxygen-18 in the reference carbon dioxide is $N_u\alpha_1 = (0.00204)(1.038) = 0.00212$. Since the enrichment, I, in an enriched sample of carbon dioxide is always determined by comparison with this reference standard, substitution of equation (3) into equation (2) gives

$$n_e = \frac{I N_u\alpha_1}{1 + N_u\alpha_1(I - 1)} = \frac{I(0.00212)}{1 + (I - 1)(0.00212)} \tag{4}$$

For enrichments not too large, $n_e \approx I N_u\alpha_1 = I(0.00212)$.

Enrichment factors. Calculation of the extent of exchange from the atom fraction n_e of oxygen-18 in the equilibrated carbon dioxide requires values for the enrichment factors at the temperatures of equilibration. These have been determined experimentally and calculated for a number of exchange reactions[15–17] of interest here. UREY's[16] calculated values for the enrichment factor $\alpha_2(g)$ for CO_2 equilibrated with water-vapour, are found to be adequately represented by $\alpha_2(g) = 1 + [(4162 \pm 124)/T^2]$. Computed values of $\alpha_2(g)$ according to this equation and at temperatures of interest in our present experiments are listed in Table 3. To obtain the enrichment factor $\alpha_2(l)$ for CO_2 and liquid water, $\alpha_2(g)$ is divided by the enrichment factor α_0 for liquid water and its vapour. α_0 is, however, equal to the ratio of the vapour-pressure, p_1, of $H_2{}^{16}O$ to the vapour-pressure, p_2, of $H_2{}^{18}O$ and was evaluated according to the relation[16] $\log(p_1/p_2) = (2.74/T) - 0.0056$. Values of α_0 and $\alpha_2(l)$ are also given in Table 3.

TABLE 3. ENRICHMENT FACTORS AS A FUNCTION OF TEMPERATURE
MS REPRESENTS THE MOLECULAR SIEVE ABSORBENTS

t (°C)	$\frac{[^{18}O/^{16}O]_{H_2O\,liq}}{[^{18}O/^{16}O]_{H_2O\,gas}}$	$\frac{[^{18}O/^{16}O]CO_2}{[^{18}O/^{16}O]_{H_2O\,liq}}$	$\frac{[^{18}O/^{16}O]CO_2}{[^{18}O/^{16}O]_{H_2O\,gas}}$	$\frac{[^{18}O/^{16}O]CO_2}{[^{18}O/^{16}O]_{MS}}$	$\frac{[^{18}O/^{16}O]_{MS}}{[^{18}O/^{16}O]_{H_2O\,gas}}$	$\frac{[^{18}O/^{16}O]_{MS}}{[^{18}O/^{16}O]_{H_2O\,liq}}$
	α_0	$\alpha_{2(liq)}$	$\alpha_{2(g)}$	α_3	α_4	α_5
25	1.0083	1.038 (α_1)	1.047	1.010	1.037	1.028
50	1.0066	1.033	1.040	1.009	1.031	1.024
80	1.0050	1.028	1.033	1.008	1.025	1.020
100	1.0040	1.026	1.030	1.008	1.022	1.018
135	1.0025	1.022	1.025	1.007	1.018	1.015
150	1.0020	1.021	1.023	1.007	1.016	1.014
250	0.9991	1.016	1.015	1.007	1.008	1.009

Calculation of extent of exchange. It is desirable to derive equations that give the extent of exchange of oxygen-18 among the species in the several different reaction systems in our experiments. Preferably these equations should be in terms of the atom fraction, n_e, of oxygen-18 in the carbon dioxide used as a monitor. We shall consider first the system $H_2{}^{18}O$–CO_2–molecular sieve adsorbents. The material balance equation for oxygen-18 in the equilibrated mixture (at 250°C) in this system is

$$am_0 + bN_0 + cn_0 = am_e + bN_e + cn_e \tag{5}$$

---

[14] H. G. THODE, *Research* 2, 154 (1949); for references to the variations in the abundance of oxygen-18 in water from various sources, see M. DOLE, *Chem. Rev.* **51**, 263 (1952), and G. BOATO, *Ann. Phys. Chem.* **6**, 403 (1955).

[15] H. C. UREY and L. J. GREIFF, *J. Amer. Chem. Soc.* **57**, 321 (1935).

[16] H. C. UREY, *J. Chem. Soc.* 562 (1947).

[17] J. BIGELEISEN and M. G. MAYER, *J. Chem. Phys.* **15**, 261 (1947).

Here, a is the mg atoms of exchangeable oxygen in the adsorbent; m_0 is the initial atom fraction of oxygen-18 in the adsorbent; b is the mg atoms of oxygen in the enriched water added to the system; N_0 is the initial atom fraction of oxygen-18 in the enriched water; c is the mg atoms of oxygen in the carbon dioxide and is equal to twice the number of millimoles of CO_2 added as a monitor; n_0 is the initial atom fraction of oxygen-18 in the carbon dioxide; m, N and n are the atom fractions of oxygen-18 in the equilibrated oxygen of the molecular sieves, the water and the carbon dioxide, respectively, at the temperature of equilibrium. In the equations that follow, the subscript 0 will refer to the initial reactants and the subscript e will refer to the values at equilibrium or at time t. Equation (5) may be solved for a to give

$$a = b\frac{N_0 - N}{m - m_0} - c\frac{n - n_0}{m - m_0} \tag{6}$$

Since n is the value obtained from the mass spectrometric analysis by Equation (4), it is convenient to express m and N in terms of n and the known enrichment factors at the temperature of the equilibration (Table 3). The enrichment factor α_2 for oxygen-18 between CO_2 and H_2O is

$$\alpha_2 = \frac{n/(1 - n)}{N/(1 - N)} \tag{7}$$

from which we get

$$N = \frac{n}{\alpha_2 - n(\alpha_2 - 1)} \approx n/\alpha_2 \tag{8}$$

When $n(\alpha_2 - 1)$ is $\ll \alpha_2$ in Equation (8) the approximate expression can be used with little error. Similarly for the adsorbents, $m = n/\alpha_3$ where α_3 is the enrichment factor for oxygen-18 between CO_2 and the exchangeable oxygen in the adsorbents. SILVERMAN[18] has estimated the enrichment factor, α, for diatomite silica in equilibrium with liquid water at 15°C as 1.030 and at 140°C as 1.014.* Using the value at 15°C and the usual relation for the variation of α with temperature one obtains $\alpha = 1 + 2490/T^2$. Calculated values of α according to this formula at several temperatures are given in Table 3. When these values are multiplied by the ratio of the vapour-pressure of $H_2^{18}O/H_2^{16}O$ the values of α_1 in Table 3 for silica relative to water vapour are obtained. The enrichment factor, α_3, of oxygen-18 for carbon dioxide in equilibrium with silica is then $\alpha_3 = \alpha_2(g)/\alpha_1$, and the values obtained are given in Table 3. We have assumed that the enrichment factors for silicate such as the molecular sieve adsorbents are the same as those for silica. The initial atom fraction of oxygen-18 in the molecular sieve adsorbents is taken as that expected for equilibrium with the water in which they were made, so that m_0 for the unused adsorbent is $N_n\alpha_1(25°C)$.

Substitution of n/α_2 for N, n/α_3 for m, $N_n\alpha_2$ for n_0 and $N_n\alpha_1$ for m_0 in Equation (6) gives

$$a = b\frac{N_0 - (n/\alpha_2)}{(n/\alpha_3) - N_n\alpha_1} - c\frac{n - N_n\alpha_2}{(n/\alpha_3) - N_n\alpha_1} \tag{9}$$

Thus, the mg atoms of exchangeable oxygen, a, is readily calculated from the known atom fraction, N_0, of oxygen-18 in the enriched water, the known normal atom fraction, N_n, of oxygen-18 in fresh water (0.00204), the known or estimated values of α_1, α_2, α_3, α, and the value of n obtained from the mass spectrometric determination of the enrichment, I, of oxygen-18 in the equilibrated carbon dioxide. Since the total gramme atoms, G, of oxygen in the adsorbents is known, the fraction of the oxygen atoms exchanged is a/G. The values listed in Table 1 were calculated in this way.

If the various values of α in Equation (9) are taken as 1.00, an approximate expression is obtained which is sometimes used in calculations for the isotope dilution method of analysis

$$a = b\frac{N_0 - n}{n_e - N_n} - c \tag{10}$$

Exchangeable oxygen by other equilibration procedures. A summary of the equations used to calculate the mg atoms of exchangeable oxygen for a number of other equilibration procedures is given in Table 4. Equation (11), for example, is used when $H_2^{18}O$ alone is equilibrated with the molecular sieve adsorbents at 250°C (Run 1a). The atom fraction, N_e, of oxygen-18 in the equilibrated water is determined as follows. The water-vapour is removed from the reaction system at the temperature of equilibration (250°C). A measured quantity, b, of the separated water is equilibrated

---

* INGERSON[19] considers 1.014 as the value at 200°C rather than at 140°C.

(18) S. R. SILVERMAN, *Geochim. et Cosmochim. Acta* **2**, 26 (1951).

(19) E. INGERSON, *Bull. Geol. Soc. Am.* **64**, 338 (1953).

TABLE 4 – EQUATIONS FOR CALCULATION OF THE Mg ATOMS OF EXCHANGEABLE OXYGEN FROM THE ATOM FRACTION OF OXYGEN-18 IN CARBON DIOXIDE OR WATER AFTER EQUILIBRATION

Reactants	Equations*	
$H_2{}^{18}O + CO_2 + MS$	$a \quad b\dfrac{N_0 \quad (n/\alpha_2)}{(n/\alpha_3) \quad N_n\alpha_5} \quad c\dfrac{n_e \quad N_n\alpha_1}{(n/\alpha_1) - N_n\alpha_1}$	(9)
	$b\dfrac{N_0 \quad n_e}{n \quad N_n} \quad c$	(10)
$H_2{}^{18}O + MS$	$a \quad b\dfrac{N_0 \quad N}{N\alpha_4 \quad N_n\alpha_4}$	(11)
$C^{18}O_2 \quad MS$	$a \quad c\dfrac{n_0 \quad n}{(n/\alpha_1) \quad N_n\alpha_5}$	(12)
$CO_2 + MS{}^{18}O$	$a \quad c\dfrac{n_e \quad N_n\alpha_1}{m_0 \quad (n_e/\alpha_3)}$	(13)
$CO_2 \quad H_2{}^{18}O$	$b \quad c\dfrac{n \quad N_e\alpha_1}{N_0 \quad (n_e/\alpha_2)}$	(14)

* See Equation (5) for the definition of symbol

with c mmole of CO_2, at 25 C and the enrichment I, in the carbon dioxide is determined from mass spectrometric measurements (Equation 1) The atom fraction n of oxygen-18 in the carbon dioxide is calculated from Equation (4) and then substituted into Equation (15) Table 5 for calculation of N N_0 in Equation (11) is the known initial atom fraction of oxygen-18 in the water, α_4 is the enrichment factor for the molecular sieve adsorbents and water vapour (1 008 at 250 C), and $N_e\alpha_5$ (25 C) is the initial atom fraction of oxygen-18 in the molecular sieve adsorbents

Since it was found that carbon dioxide exchanges oxygen atoms with the molecular sieve adsorbent at elevated temperatures, $C^{18}O_2$ can be used in the place of $H_2{}^{18}O$ to determine the exchangeable oxygen Equation (12) is used in this case, where α_1 is the enrichment factor for CO_2 and the molecular sieve adsorbent (1 007 at 250 C), N_0 is the known initial atom fraction of oxygen-18 in the carbon dioxide and $N_n\alpha_5$ (25 C) is the initial atom fraction of oxygen-18 in the exchangeable oxygen of the molecular sieve adsorbent

If the molecular sieve adsorbent has been previously enriched in oxygen-18 the mg atoms of exchangeable oxygen can also be determined by equilibration with carbon dioxide (See Run 1-b Table 1) Equation (13) is used for these calculations where α_1 is the enrichment factor for CO_2 and the molecular sieve adsorbent at the temperature of equilibration (1 007 at 250 C) and m_0 is the known initial atom fraction of oxygen-18 in the exchangeable oxygen of the molecular sieve adsorbent A similar equation (Equation 14) is used to calculate the number of mg atoms of oxygen in an enriched sample of water In such measurements it is desirable though not necessary that the mg atoms of oxygen in the carbon dioxide be of the same order of magnitude as the mg atoms of exchangeable oxygen in the molecular sieve adsorbent or in the water

Determination of the atom fraction of oxygen-18 A number of the experiments required the determination of the atom fraction of oxygen-18 in a particular species The equations for these calculations are summarized in Table 5 Equation (15) for example is used to calculate the initial atom fraction of oxygen-18 in enriched water (See Run 5) A small quantity of carbon dioxide is equilibrated with the enriched water and the atom fraction, N, of oxygen-18 is determined from the mass spectrometer analyses using Equation (1) and Equation (4) α_2 is the enrichment factor for the temperature of equilibration but α_1 (1 038) is the enrichment factor for CO_2 and water at 25 C because the equilibrated CO_2 is always compared with tank carbon dioxide whose atom fraction of oxygen-18 is $N_n\alpha_1$ (See Equation (3a) A similar procedure [See Equation (16)] is used to determine the initial atom fraction of oxygen-18 in the exchangeable oxygen of the molecular sieve adsorbents

When it is desired to calculate the atom fraction and enrichment, I of oxygen-18 expected in carbon dioxide after equilibration with enriched water, Equation (17) and (18) are used Equations) and (18) apply if enriched molecular sieve adsorbents are used in the place of enriched water values in parentheses in Tables 1 and 2 were calculated in this way

TABLE 5. SUMMARY OF EQUATIONS FOR CALCULATION OF THE ATOM FRACTIONS OF OXYGEN-18

Reactants	*Equation*	
$CO_2 + H_2^{18}O$	$N_0 = (a + $ [illegible] $(c + b\alpha_1 + $ [illegible] $N\alpha_1)$	(15)
$CO_2 + MS^{18}O$	$m_0 = (a + c\alpha_1)$ [illegible] $(c + a)n$ [illegible] $N\alpha_1)$	(16)
$CO_2 + H_2O$	$n = \frac{bN}{(b + c)} + \frac{cN\alpha_1}{c}$	(17)
	$t = \frac{n(1 - N\alpha_1)}{N\alpha_1(1 - n)}$	(18)
$CO_2 + MS^{18}O$	$n = \frac{am_0}{(a + c)} + \frac{cN\alpha_1}{c}$	(19)
$C^{18}O_2 + H_2^{18}O$	$N = \frac{n}{\alpha_2 - n(\alpha_2 - 1)}$	(20)
$H_2O + MS^{18}O$	$m = \frac{N\alpha_1}{1 + N(\alpha_1 - 1)}$	(21)
$H_2^{18}O + C^{18}O_2 + MS^{18}O$	$m = \frac{n}{\alpha_3 - n(\alpha_3 - 1)}$	(22)
$H_2^{18}O + CO_2 + MS$	$n = \frac{aN_0\alpha_3 + bN_0 + cN_1\alpha_1}{a\alpha_3 + b\alpha_2 + c}$	(23)

See Equation (5) for definition of symbols

If the atom fraction of oxygen-18 at equilibrium is known for any one species, the atom fraction of oxygen-18 in one of the other species may be calculated from Equations (20), (21) or (22). The values of α_2, α_3 and α_1 are for the temperature of the equilibration. Thus when carbon dioxide is used as a monitor in the equilibration of a mixture of CO_2, $H_2^{18}O$ and the molecular sieve adsorbent, the atom fraction of oxygen-18 in the adsorbent can be calculated directly from the atom fraction n of oxygen-18 in the carbon dioxide without consideration of the water. The value of n, can be determined experimentally from the mass spectrometric analysis of the carbon dioxide [Equations (1) and (4)]. Alternatively n may be calculated since it is related to the total mg atoms of exchangeable oxygen through the material balance equation [Equation (5)], as shown in Equation (23).

The equations summarized in Tables 4 and 5 should be generally useful for other similar investigations. Some of the equations are similar to those used by others[20-29], except that the ones derived here are in a form which readily takes into account the temperature of equilibration and the usual method of mass spectrometric analysis. Enrichment factors are more convenient to use than equilibrium constants and are more frequently listed in tables of experimentally determined or theoretically calculated values.

---

(20) M. COHN and H. C. UREY, *J. Amer. Chem. Soc.* **60**, 679 (1938).

(21) W. H. MEARS and H. SOBOTKA, *J. Amer. Chem. Soc.* **61**, 880 (1939).

(22) D. RITTENBERG and G. L. FOSTER, *J. Biol. Chem.* **133**, 737 (1940).

(23) H. GEST, M. KAMEN and J. M. REINER, *Arch. Biochem.* **12**, 273 (1947).

(24) R. BENTLEY, *Nucleonics* **2**(2) 18 (1948).

(25) H. R. V. ARNSTEIN and R. BENTLEY, *Quart. Rev. Chem. Soc.* (London), **4**, 172 (1950).

(26) A. V. GROSSE, S. G. HINDIN and A. D. KIRSHENBAUM, *Analyt. Chem.* **21**, 386 (1949).

(27) I. DOSTROVSKY and F. S. KLEIN, *Analyt. Chem.* **24**, 414 (1952).

(28) S. L. JONES and N. R. TRENNER, *Analyt. Chem.* **28**, 387 (1956).

(29) R. N. BOOS, S. L. JONES and N. R. TRENNER, *Analyt. Chem.* **28**, 390 (1956).

DISCUSSION

The results of experiment 1 (Table 1) show that both H_2O and CO_2 exchange oxygen-18 with the molecular sieve adsorbents at 250 C. The enrichment, *E*, for the CO_2 is practically the same, whether the CO_2 is equilibrated with the water or with the adsorbents after completion of the reaction. This result indicates that H_2O and CO_2 exchange with about the same fraction of oxygen atoms in the molecular sieve adsorbents. The mechanism of the exchange of the CO_2 with the molecular sieve adsorbents is probably through small quantities of water not removed by ordinary evacuation. According to this mechanism the carbon dioxide exchange would be expected to measure essentially the same exchangeable oxygens as the water does. When the enriched molecular sieves were dried by evacuation at 250 C for longer periods of time, as in experiments 6 and 7 (Table 2), the exchange with carbon dioxide was somewhat slower and did not reach the expected value in one to two hours.

In experiment 2 (Table 1), the extent of exchange was determined as a function of time at 250 C. The results show that a rapid exchange of about 75 per cent of the oxygen in the molecular sieve is completed in about one hour, followed by a further slow exchange to about 82 per cent in 24 hr. This is similar to the results of MILLS and HINDIN(8), and OBLAD *et al.*(9) on silica alumina catalysts. The mechanism assumed to explain their results involved a rapid exchange of surface oxygen through reversible hydrolysis of metal oxygen bonds. For oxygen below the surface, a slower exchange process occurs as a result of diffusion of water molecules through the network of channels. Although the passages in the silica alumina catalysts are just large enough to admit oxygen ions, they postulated that lattice vibrations at the higher temperatures (450 C) might be sufficient to allow passage of water molecules or hydroxyl ions. Such an exchange process could occur with only momentary distortion of the lattice and result in a chain-like effect being transmitted from one silicon oxygen tetrahedron to the next. Since the molecular sieve adsorbents have a more open structure and a greater fraction of surface oxygens available to water in the cavities, the rate and extent of exchange should, as observed, be somewhat greater than for the silica-alumina catalysts. The results for the molecular sieve adsorbents suggest that probably a somewhat similar exchange mechanism is involved.

At lower temperatures (150 and 135 C), the exchange reaction was much slower and only 38 per cent of the oxygen atoms exchanged in 145 hr. The activation energy estimated from the results between 250 and 150 C is about 24 kcal/mole. That the rate of exchange between water and the carbon dioxide used as a monitor was not limiting, was demonstrated by the following separate experiments. When CO_2 was equilibrated at 25 C with 0.3 ml of 1.5% $H_2{}^{18}O$ in a 20 ml reaction vessel the time for one-half equilibration was about 2 hr. In the presence of 50 mg of the molecular sieve adsorbent, the time for one half equilibrium under otherwise similar conditions was 10 min. Thus, the molecular sieve adsorbents serve as an effective catalyst for the oxygen-18 exchanges between carbon dioxide and water. At higher temperatures the exchange should be considerably more rapid and consequently the carbon dioxide es as a continuous monitor of the oxygen-18 exchange between the water and the lecular sieve adsorbents.

Experiments 8 and 9 (Table 2) indicate very little exchange at 26 and 80 C between carbon dioxide and the dry molecular sieve adsorbents enriched in oxygen-18. Thus, g the molecular sieves at 250 C under high vacuum leaves very little water as exchangeable H_2O molecules. The molecular sieve adsorbents were enriched by equilibration with $H_2{}^{18}O$ at 250°C and apparently the small quantity of water left at higher temperatures arises from the OH groups formed when water reacts at 250°C with the adsorbents.

Our experiments have demonstrated that oxygen-18 exchange occurs readily between water and the molecular sieve adsorbents at the temperatures used in their regeneration. In order to use them for removal of water vapour in the exit gases from the reflux system of our isotope separation columns, the quantity needed should be not so large as to markedly increase the moles of exchangeable oxygen. The relatively high capacity for adsorption of water made it possible to reduce the quantity of adsorbent to about 15 g. The oxygen-18 contained in them at the end of the run could be recovered in part by exchange with carbon dioxide or with water.

Although nitrogen gas was used for back-flushing the molecular sieve adsorbents during their regeneration, it was important to know whether or not a gas containing oxygen could also be used. Exchange between oxygen gas and the molecular sieve adsorbents would dilute the oxygen-18. Experiments 10 and 11 (Table 2) on dry and wet molecular sieve adsorbents indicate negligible exchange with oxygen gas at 250°C, the temperature of regeneration. Consequently, it was not necessary to use oxygen free gas for the regeneration.

J. Inorg. Nucl. Chem. 1963, Vol. 25, pp. 271 to 282. Pergamon Press Ltd. Printed in Northern Ireland

ION-EXCHANGE PROPERTIES OF ZIRCONYL PHOSPHATES—III

INFLUENCE OF TEMPERATURE ON TRACER ION EQUILIBRIA

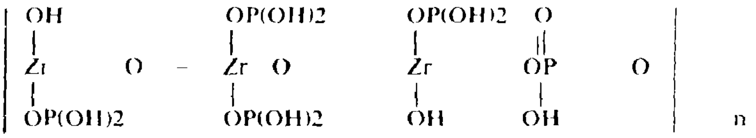
L. BAETSLÉ
Waste disposal Research Laboratories C.E.N. Belchim, Belgian Nuclear
Research Center, Mol, Belgium

(*Received 1 June 1962; in revised form 30 July 1962*)

Abstract—The influence of temperature on the ion exchange reactions of zirconyl phosphate in the H-form with Rb, Cs, Ca, Sr, Ce and Eu has been studied. It appears that Rb and Cs are very strongly adsorbed at room temperature but easily eluted at 80–100°C. The other nuclides investigated do not show such properties.

The thermodynamic quantities ΔG, ΔH and ΔS of the reactions are derived and throw some light on the exchange mechanism of the different ions studied, particularly of the alkali metal ions.

A SERIES of studies[1,2] has led to a better understanding of the structure and ion exchange properties of some zirconyl phosphates (ZrP). A semi-crystalline compound with a P/Zr ratio of 5/3 was found, having a total exchange capacity of 4.5 meq/g and a pK of about 3.7. The suggested structure is based on the trimer form of the zirconyl salts in 5 N HCl solution, which reacts with the environmental phosphate ions.



$$\left[\begin{array}{ccccccc} \text{OH} & & \text{OP(OH)2} & & \text{OP(OH)2} & \text{O} & \\ | & & | & & | & \| & \\ \text{Zr} & \text{O} - & \text{Zr} & \text{O} & \text{Zr} & \text{OP} & \text{O} \\ | & & | & & | & | & \\ \text{OP(OH)2} & & \text{OP(OH)2} & & \text{OH} & \text{OH} & \end{array}\right]_n$$

Above pH 7 the product loses its stability and phosphate ions enter the solution leaving an acid soluble Zr oxyde. However, many other compounds with variable properties can be obtained by precipitating zirconyl salts and phosphates in dilute acid and neutral conditions[3] but the structure of the obtained slurries is obscure. The main interest of the use of ZrP lies in the field of nuclear chemistry and ion exchange processes at high temperature due to its high affinity for Cs and Rb on the one hand and its irradiation and thermal stability on the other hand.[4,5]

The affinity of Cs$^+$ and Rb$^+$ for the functional groups of ZrP is so high that they can be eluted with 5 N HNO_3 only with difficulty, an acid concentration which is inconveniently strong.

The present report concerns the influence of temperature on the equilibria Cs–H, Rb–H, Sr–H, Ca–H, Eu–H, and Ce–H with respect to ZrP in HNO_3 solution.

Several studies of the temperature dependence of ion exchange reactions on

---

[1] L. BAETSLÉ and J. PELSMAEKERS *J. Inorg. Nucl. Chem.* **21**, 124–132 (1961).

[2] L. BAETSLÉ and D. HUYS *J. Inorg. Nucl. Chem.* **21**, 133–140 (1961).

[3] R. J. CHIDLEY and J. R. GROVER, Report AERE/R/3357 (1960).

[4] K. A. KRAUS, H. O. PHILLIPS, T. A. CARLSON and J. S. JOHNSON, *The Proceedings of the Second International Conference on Peaceful Uses of Atomic Energy*, Geneva 1958, Vol. 28, p. 3. United Nations (1958).

[5] C. B. AMPHLETT, *The Proceedings of the Second International Conference on Peaceful Uses of Atomic Energy*, Geneva 1958, Vol. 28, p. 12. United Nations (1958).

synthetic organic resins have been made by several authors.[6–9] The first study on this subject in relation with ZrP has been published recently and deals with the equilibria Li–H, Na–H and K–H.[10]

EXPERIMENTAL

The ZrP prepared by the method described in[2] leads to a product with well known characteristics. A certain amount (0.25 g) of ZrP in the hydrogen form was added to 50 ml of HNO_3 solution containing between 0.001 and 0.5 N HNO_3 and tracer quantities of ^{134}Cs, ^{86}Rb, ^{89}Sr, ^{45}Ca, ^{152}Eu and ^{144}Ce. The radionuclides were all carrier free except ^{45}Ca which was accompanied with 12 p.p.m. of inactive Ca per $4 \cdot 10^4$ disintegrations per minute.

After 24–48 hr stirring in a thermostatic bath, the solution was filtered immediately (in order to prevent a t change) and was counted afterwards in a G.M. or scintillation counter. The equilibria were investigated at 16, 30, 50 and 70°C with a deviation of 1°C at most. Below 50°C 48 hr contact was necessary to reach full equilibrium; above 50°C a contact time of 24 hr was sufficient.

From the difference between the initial-(C_i) and the equilibrium activity (C_e) it is possible to calculate the distribution coefficient

$$Kd = \frac{C_i - C_e}{C_e} \text{ ml g}^{-1}$$

RESULTS

(a) *Monovalent tracer equilibria.* The ion exchange relationship between Cs and Rb with respect to ZrP in the H-form was investigated in the HNO_3 concentration 0.01 to 0.5 M between 5 and 70°C. The results are presented in Figs. 1 and 2.

(b) *Bi-monovalent tracer equilibria.* The behaviour of Ca^{2+} and Sr^{2+} was studied at very low concentrations where a linear relationship exists between log K_d and log (HNO_3) i.e. between 0.005 and 0.02 M HNO_3. The results of the equilibria are given in the Figs. 3 and 4.

(c) *Tri-monovalent equilibria.* The fixation of Eu^{3+} and Ce^{3+} in 0.01 to 0.1 M HNO_3 at the same temperatures is shown in Figs. 5 and 6.

THEORETICAL CONSIDERATIONS

Although the influence of the temperature on ion exchange reactions with synthetic organic resins is relatively small,[6–9] only low temperatures can be used because of the lack of thermostability of the resins. With mineral exchangers such thermal damage does not exist, but hydrolysis effects may affect the adsorption characteristics at very high temperatures.

The thermodynamic relationships which form the basis of ion exchange reactions at different temperatures have been reviewed recently by Kraus[9] who uses the data of Lietzke[11] for calculating the activity coefficients in the aqueous phase at elevated temperatures. The mathematical relation between the selectivity coefficient, the mass action constant, the concentrations (in meq) and activities of the ions in the tracer exchange reaction

$$bA^{a} + aR_{b}B \rightleftharpoons aB^{b} + bR_{a}A \qquad (1)$$

---

[6] N. T. Coleman, *Soil Sci.* **74**, 115 (1952).

[7] E. H. Cruickshank and P. Meares, *Trans. Faraday Soc.* **53**, 1289 (1957); **54**, 174 (1958).

[8] K. A. Kraus, R. J. Raridon and D. L. Holcomb, *J. Chromatography* **3**, 178–189 (1960).

[9] K. A. Kraus and R. J. Raridon, *J. Phys. Chem.* **63**, 1901 (1959).

[10] E. M. Larsen and D. R. Vissers, *J. Phys. Chem.* **64**, 1732 (1960).

[11] M. H. Lietzke, Tables of the activity coefficient of a 1–1 electrolyte and its derivatives calculated using a modified Debye Huckel equation, ORNL 2628 (Dec. 1958).

where A^{a+} is the tracer component and B^{b+} the macrocomponent with valences *a* and *b* respectively, is given by the relation

$$K' = K'''\Gamma(aq) = (K_d)_A^{1/a} \left\{\frac{M_B}{Q}\right\}^{1/b} \Gamma(aq) \tag{2}$$

In this formula the following symbols are used

K'	selectivity coefficient,
K'''	mass action constant,
$(K_d)_A$	distribution coefficient of the tracer component A,
M_B	the molar concentration of the macrocomponent B
Q	the total exchange capacity (= 4.5 meq/g),
$\Gamma(aq)$	the ratio of the activity coefficient in the aqueous phase

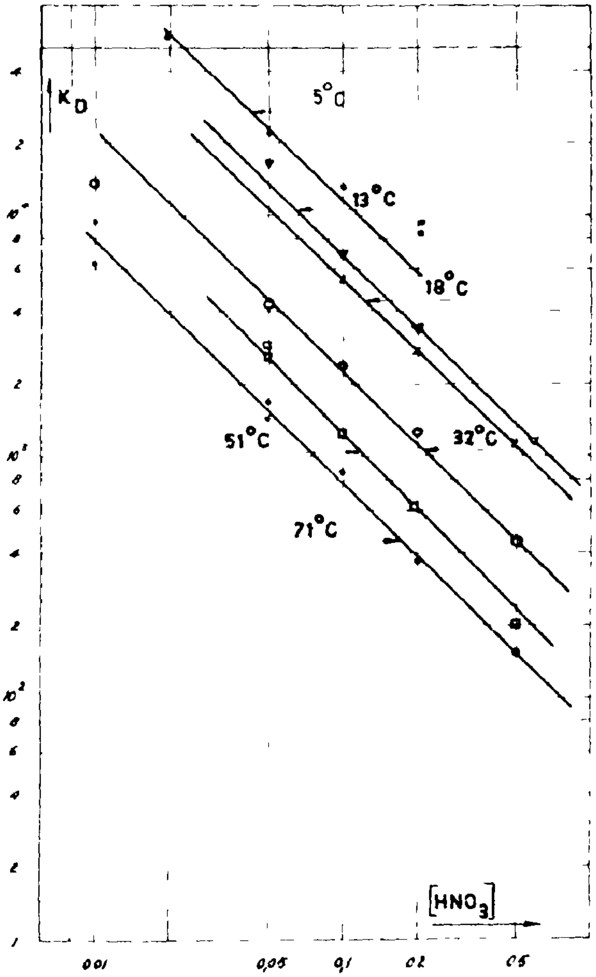


FIG 1 —Influence of temperature on the fixation of Cs on zirconyl phosphate

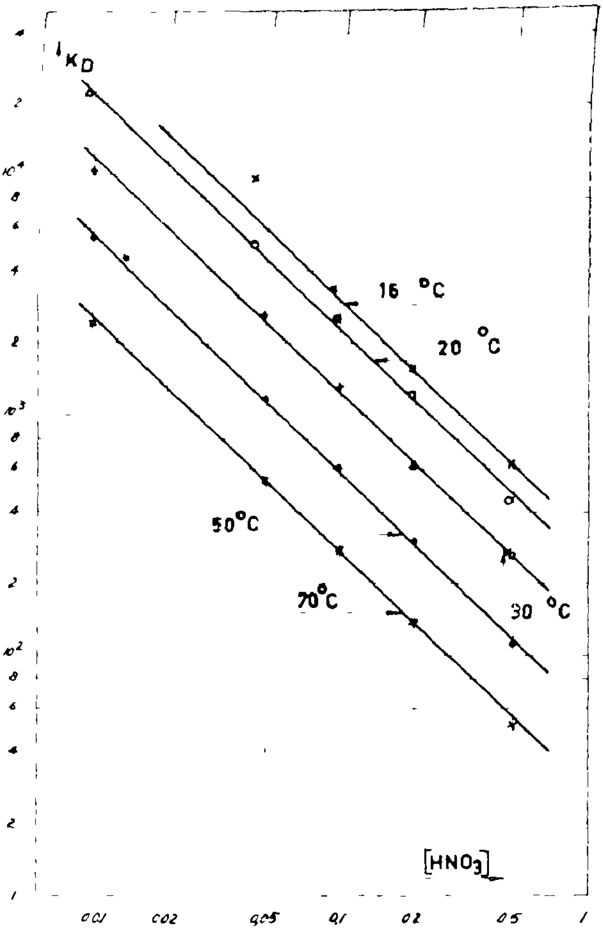


FIG. 2 – Influence of temperature on the fixation of Rb on zirconyl phosphate

The tables of LIETZKE give the values of the mean activity coefficients ($\gamma_\pm$) using the following expression

$$\log \gamma_\pm = -\left(\frac{\rho_s}{D^3 T^3}\right)^{\frac{1}{2}} \frac{S_0 \sqrt{(\mu)}}{1 + A' \sqrt{(\mu)}} = F_1 S_0 f(\mu) \tag{3}$$

where

ρ_s – the density of water,

D – the dielectric constant of water

S_0 = 1.8252×10^6

A' – (= 1.5) a constant related with the distance of closest approach of the ions in solution,

μ = the ionic strength of the solutions = $\frac{1}{2}\Sigma M_x z_x^2$

F_1 – $\left(\frac{\rho_s}{D^3 T^3}\right)^{\frac{1}{2}}$

In the case of 1–1 exchanges $K' = K''$, in multivalent exchange a correction has to be applied for the activity of the components in the solution. A few empirical relations have already been put forward by some authors in order to provide a mathematical description of the temperature influence on the selectivity coefficients (8,9)

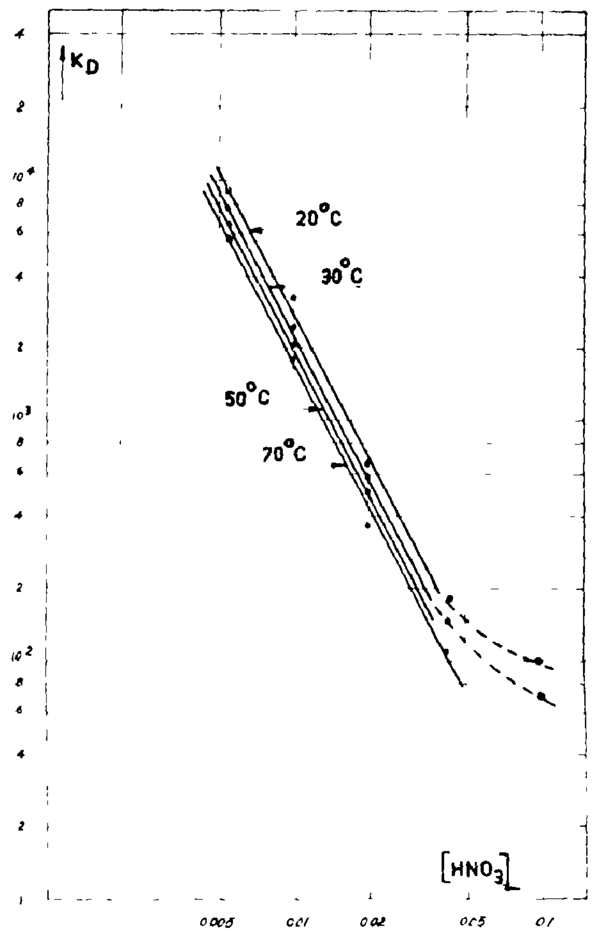


FIG. 3. Influence of temperature on the fixation of Ca on zirconyl phosphate

In addition to the classical equation

$$\log K = C_1 - \frac{C_2}{T} \tag{4}$$

one encounters the three parameter expression

$$\log K' = C_1 - \frac{C_2}{T} + C_3 \log T \tag{5}$$

Very recently a more elaborate formula has been suggested by KRAUS(9)

$$\log K' = \log K_0 + \alpha \log T/T_0 + \beta(1 - T_0/T) \tag{6}$$

The Equations (5) and (6) are thermodynamically equivalent but in Equation (6) a reference constant K_0 (at temperature T_0) is introduced. The latter fact has the disadvantage that at a given temperature T_0 the value of K_0 must be known very accurately, which is not always possible experimentally.

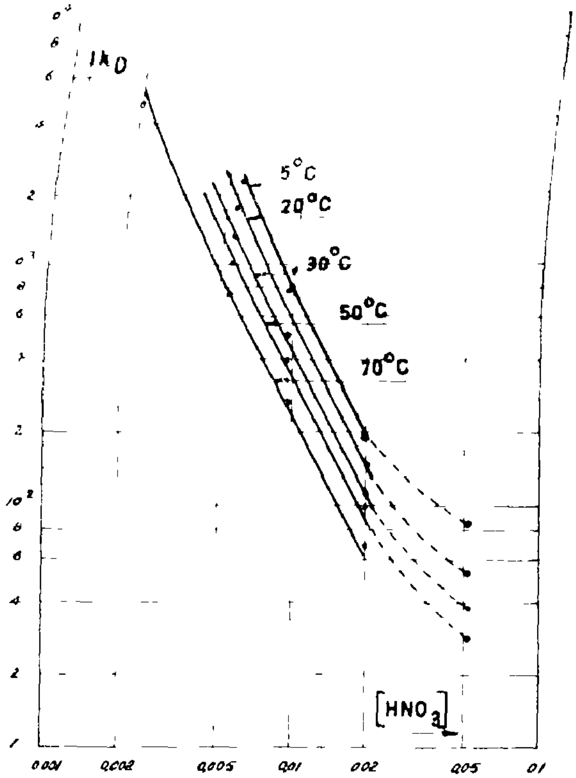


FIG. 4. Influence of temperature on the fixation of Sr on zirconyl phosphate.

THERMODYNAMIC EQUILIBRIUM DATA

The selectivity coefficients as a function of temperature were calculated from the results of experiments carried out with Rb^+, Cs^+, Ca^{2+}, Sr^{2+}, Eu^{3+} and Ce^{3+} at different temperatures. The best fitting curves have been computed on the "Mercury" digital computer.* The results are given in Table 1 and plotted in Fig. 7.

The parameters of the best fitting equations are given in Table 2 together with the derived thermodynamic data ΔG, ΔH and ΔS.(12, 13)

DISCUSSION

The choice of the best fitting equations has been made by computing the mean standard deviation and by calculating the dispersion factors on the parameters C_1, C_2 and/or C_3.

As can be deduced from the experimental results in Table 1, the three parameter equation describes quite well the variation of K' with temperature for the systems Rb H⁺ and Cs⁺ H⁺ For all other systems a linear relationship is found between log K' and $1/T$ which indicates, within the limits of measurement errors, the constancy of the enthalpy ΔH and of the entropy ΔS over the whole range of temperatures studied

---

* The author is very indebted to Dr SCHOTSMANS of the Applied Mathematics section for aid in the computations and programming of the experimental data.

(12) G. E. BOYD, J. SCHUBERT and A. W. ADAMSON, *J. Am. Chem. Soc.* **69**, 2829 (1947).

(13) H. S. HARNED and B. B. OWEN, The physical Chemistry of electrolytic solutions, Reinhold Publication Co., Second Edit. 1958 pp. 644.

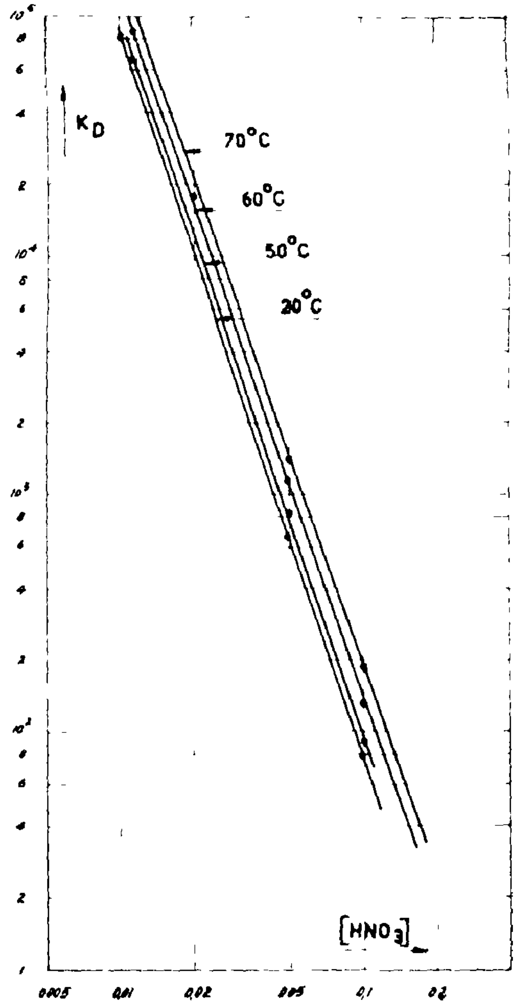


FIG. 5 - Influence of temperature on the fixation of Ce on zirconyl phosphate

Moreover the variation of K' which is very important for Rb and Cs is small for the trivalent ions Eu^{3+} and Ce^{3+} and negligible for the alkaline earth metals Ca^{2+} and Sr^{2+} It is worth noting that the temperature coefficient for the rare earths exchanges s of the opposite sign to that for the alkali metals and alkaline earths

The enthalpies and entropies of the exchange reactions of the tri- and bivalent ions ZrP are of the same order of magnitude as those found for sulphonated polystyrene ins with a high degree of cross linking (7, 9, 14)

---

(9) D Bonner *et al*, *J Phys Chem* **61**, 1614 (1957) **63**, 1417 and 1421 (1959) **65**, 1599 (1961)

For Rb^+ and Cs^+ the picture is completely different, the excess free energy which is the driving force of the reaction is very high compared to that for the analogous reactions of sulphonate resins[9] ($\Delta G_{Cs,H} = -1.21$, $\Delta G_{Rb,H} = -0.99$ at 25 C). On the other hand it must be emphasized that the selectivity of ZrP seems to be limited

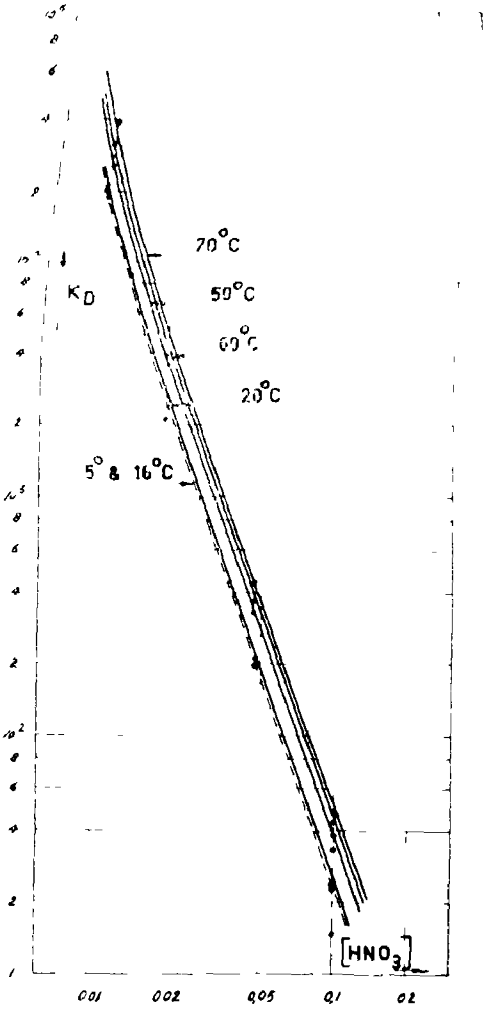


FIG. 6 — Influence of temperature on the fixation of Eu on zirconyl phosphate

to both heavy alkaline metals in acid medium. Indeed the sign of ΔG varies from + for Li, Na and K to − for NH_4, Rb and Cs as can be seen in the sequence of affinity of the alkali metals given in Table 3 where the data of LARSEN[10] are presented together with the present results.

It appears therefore that the affinity series of the alkali metals differs strongly from the sequence found for pure weakly acidic exchange functions where H^+ has the highest affinity. The exchange properties of ZrP lie between these of the weak and strong acid functional groups which confirms the earlier hypothesis of the secondary phosphate functions with a *pK* of 3.7.

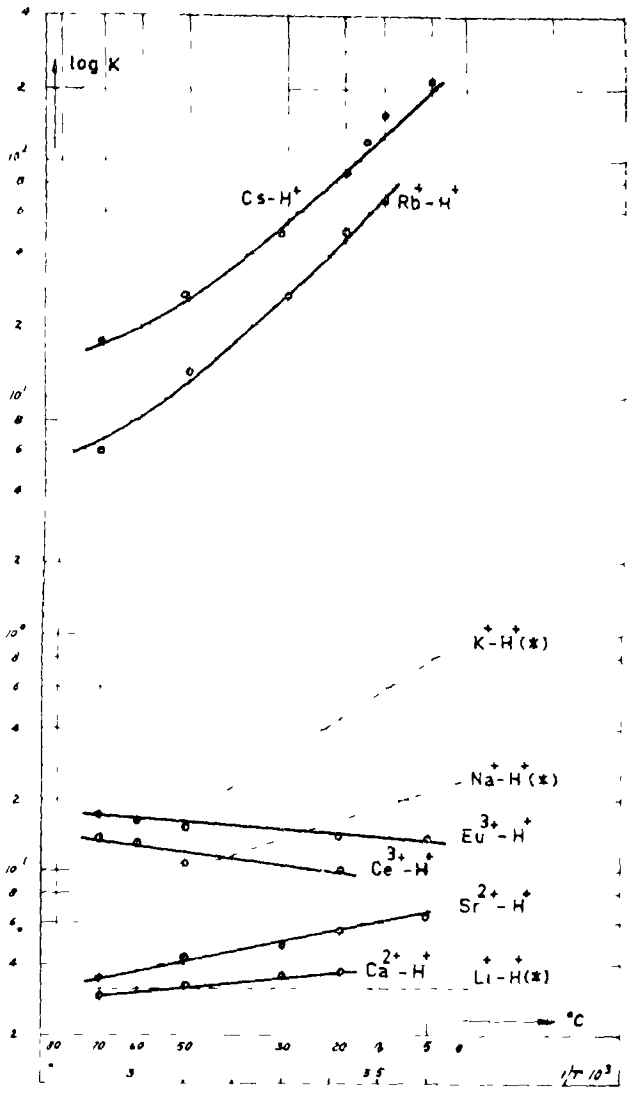


FIG. 7 – Influence of temperature on selectivity constants

The affinity series may be written as follows

Li Na K H NH$_4$ Rb Cs

The relation between the relative entropies of the aqueous ions(15) and the entropy of exchange put forward by LARSEN(10) exists also for Rb and Cs. Another interesting relationship can be found between the exchange entropies and the ion size of the non-hydrated alkali-ions as plotted in Fig. 8. This can be interpreted as an exchange of the covalently bound H$^+$ for a non hydrated alkali-ion. Using the known hydrated-ion size, no correlation whatsoever was found. The behaviour of ZrP with respect to the ion exchange of alkali metals as non-hydrated ions(16) can be ascribed to the

---

W. M. LATIMER, *Oxidation potentials*, Prentice Hall, New York N.Y. (1952)

VON HELFFERICH, *Ionenaustauscher Band I* p. 184 Verlag Chemie, Weinheim (1959) semicrystalline structure of the material A similar adsorption sequence based on the non hydrated ionic radii is also found in the case of synthetic zeolites (16 17 18)

The physical picture of the exchange can be thought of as follows, the hydrated ions in the interstitial liquid react with the covalently bound hydrogen ion The reaction affinity is inversely proportional to the degree of hydration, during the exchange the

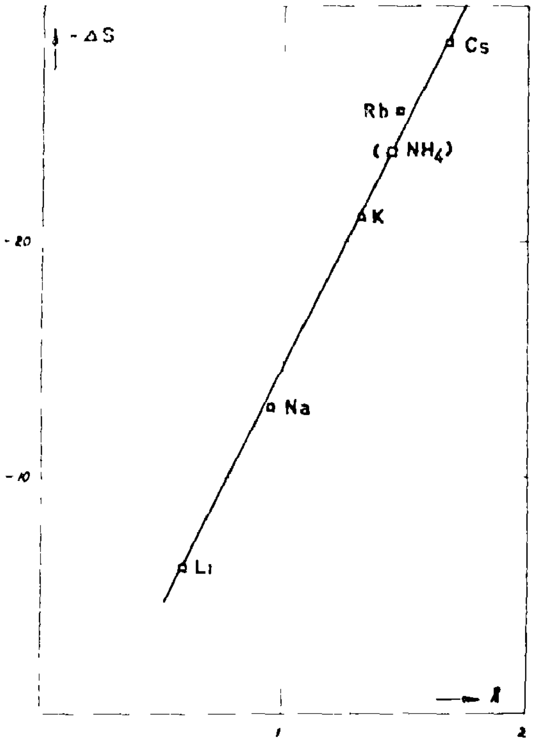


FIG. 8 Exchange entropy as a function of ion size

polarized hydration shell is displaced but at the same time the liberated hydrogen ions become hydrated The exchange entropy is consequently made up of two factors the entropy decrease due to the stronger fixation of the exchanging ions and the entropy difference between the hydrated exchanging and the hydrated exchanged ions The overall difference in entropy is also less for the very large hydrated ions Li^+ and Na^+ than for K^+, Rb^+ and Cs^+ which are almost free of water of hydration

The enthalpies of the reactions studied are again much higher than those found for sulphonated polystyrene resins (14) This suggests a much stronger chemical bond between the alkali metals and the phosphate groups than in the case of sulphonate groups

The exchange mechanism of ions on ZrP, described above, is similar to the one observed for synthetic zeolites, although not identical On the one hand the constancy of the selectivity constant over a relatively wide range of concentrations in the external

---

(17) R M BARRER, *Proc Roy Soc* **236** A, 227 (1956)

(18) R M BARRER, *Proc Roy Soc* **238** A, 299 (1958)

solutions and the fixation on the functional group as non-hydrated ions are two factors which suggest a "synthetic zeolite" mechanism, on the other hand the "ion sieve" properties of the zeolites have not been found for the alkali metals on ZrP. An investigation of the adsorption sequence of cations of very large size, such as tetramethyl and tetraethyl ammonium, might indicate if "ion sieve" action can be found.*

TABLE 1.—SELECTIVITY COEFFICIENTS OF SOME TRACER-ION EXCHANGE REACTIONS ON ZrP AS A FUNCTION OF TEMPERATURE

T	Rb-H K_{Exp}	Rb-H $K'(4)$	Rb-H $K'(5)$	Cs-H K'_{Exp}	Cs-H $K(4)$	Cs-H $K'(5)$	Ca-H K'_{Exp} ×100	Ca-H $K(4)$ ×100	Ca-H $K(5)$ ×100
278			-	215.0	196.0	212.0			
286	66.0	70.6	63.2	156.0	133.4	150.6	–	-	
290				120.0	112.2	116.2		--	-
293	50.0	49.4	50.2	89.0	97.4	96.9	3.69	3.69	3.67
303	27.5	30.4	29.6				3.48	3.51	3.51
305				50.0	59.6	52.0		-	–
323	12.7	9.9	12.2	-			3.24	3.22	3.22
324				27.8	29.2	26.1			
333				-					
343	6.0	5.7	6.0				2.96	2.98	2.97
344				17.1	15.0	17.4	-	–	-

T	Sr-H K_{Exp} ×100	Sr-H $K(4)$ ×100	Sr-H $K(5)$ ×100	Ce-H K'_{Exp}	Ce-H $K'(4)$	Ce-H $K(5)$	Eu-H K_{Exp}	Eu-H $K(4)$	Eu-H $K(5)$
278	6.27	6.23	6.30				0.140	0.133	0.144
286	-	—						-	-
290			-	0.098	0.099	0.100	0.140	0.140	0.139
293	5.57	5.52	5.49	0.104	0.102	0.100	0.141	0.142	0.141
303	4.86	5.0	5.01	-					
305									
323	4.31	4.01	4.21	0.112	0.118	0.113	0.154	0.157	0.154
324	-								
333				0.123	0.126	0.123	0.162	0.162	0.161
343	3.54	3.58	3.57	0.139	0.133	0.137	0.168	0.167	0.168
344									

Summarizing, one might say that only two ions have really a strong affinity for ZrP. This interesting but particular selectivity may be attributed to the specific interactions between the undissociated phosphate group and the heavy almost unhydrated alkaline metal ions Rb and Cs. The selectivity constants of the bivalent ions are very low in an acid medium but are quite high in a neutral medium (pH 5–7)(2).

The selectivity change is probably due to the hydrolysis of the alkaline earth ions n neutral solution ($Sr^{2+} + H_2O \rightleftharpoons SrOH^{+} + H^{+}$). The trivalent ions show a higher finity for ZrP than the bivalent ions.

Finally, the strong temperature dependence of the equilibrium Cs–H must be ssed because of its great importance in the elaboration of an economical system the separation of ^{137}Cs from Fission Product Solutions.

---

* *Added in proof.* This particular point was treated in a note by C. B. AMPHLETT and L. A. DONALD, *Proc. Chem. Soc.* 276 (1962).

PRACTICAL APPLICATIONS IN THE RADIOCHEMICAL FIELD

Many applications have already been suggested for ZrP by several authors(4, 5, 19) the main one being the separation of Cs from mixed fission products solutions and eventually ion exchange at elevated temperatures in water-cooled nuclear reactors. Other possible applications are in the fields of analytical(20) and preparative chemistry, e.g. the determination of the Cs content in natural waters, the separation of rare earths and trans-plutonium elements and finally the purification of Cs and Rb salts which are of increasing importance in new technological applications.

TABLE 2. PARAMETERS OF THE FITTING EQUATIONS (4) (5) AND DERIVED THERMODYNAMIC DATA AT 20 °C

System	Equation (4) C_1	Equation (4) C_2	Equation (5) C_1	Equation (5) C_2	Equation (5) C_3	Used Eqn	ΔG (kcal/equiv)	ΔH (kcal/equiv)	ΔS (cal/°C equiv)
Rb–H	4.706	1.876	72	8.051	[illegible]	(5)	2.78	9.56	24.8
Cs–H	.486	−1.606	205	10.880	68.3	( )	2.60	10.01	25.0
Ca–H	2.071	186	1.93	5.587	1.18	(4)	1.91	0.86	9.3
Sr–H	2.840	575	6.17	2.87	2.97	(4)	1.69	1.72	11.1
Ce^{3}–H	0.205	2.2	80.1	3.475	27.2	(4)	1.34	1.06	0.95
Eu^{3}–H	0.862	143	20.8	−808.6	6.98	(4)	1.14	0.65	1.67

TABLE 3. – THERMODYNAMIC DATA OF THE ALKALIMETALS EXCHANGE ON ZIRCONYL PHOSPHATE (AT 14 °C)

	Li	Na	K	NH_4	Rb	Cs
ΔG (kcal/equiv.)	2.0*	1.10*	0.56*	(1.92)†	2.36	2.86
ΔH (kcal/equiv.)	0.00*	2.70*	5.70*		9.74	10.96
ΔS (cal/°C/equiv.)	6.07*	13.0*	21.0*	(24)†	−25.2	28.3
Ion Size (Å)	0.60	0.95	1.33	1.42	1.48	1.69
Aqueous (20 °C) Entropy	3.4	14.4	−24.5		29.7	31.8

* Data of LARSEN

† Calculated values

Acknowledgements – I wish to thank first my collaborators Mr. HUYS and Mr. PEETERS for their accurate work in the laboratory. I am very much indebted to Dr. M. D'HONT, Dr. P. DEJONGHE and Dr. P. SCHONKEN for their constructive criticisms during the preparation of the manuscript.

(19) C. B. AMPHLETT, L. A. McDONALD, M. J. REDMAN *J. Inorg. Nucl. Chem.* **6**, 220 (1958).
(20) C. B. AMPHLETT, L. A. McDONALD, J. S. BURGESS, J. C. MAYNARD, *J. Inorg. Nucl. Chem.* **10**, 69 (1959).

J. Inorg. Nucl. Chem. 1963, Vol. 25, pp. 283 to 290. Pergamon Press Ltd. Printed in Northern Ireland

AQUEOUS SYSTEMS AT HIGH TEMPERATURE—VIII

THE SOLUBILITY OF UO_3 HYDRATES IN HNO_3–H_2O SOLUTIONS, 25–350°C, 10^{-4}–6 MOLAL NITRATE*(1)

WILLIAM L. MARSHALL and RUTH SLUSHER
Reactor Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee

(Received 23 July 1962)

Abstract—The solubility of UO_3 hydrates in HNO_3–H_2O solutions in the presence of the vapour was determined at temperatures from 25 to 350°C and at concentrations of total nitrate varying from 10^{-4} to 6 molal. The saturation molal ratios, $m_{UO_3}/m_{N_2O_5}$, were found to decrease from 2.6 to 0.32, from 1.60 to 0.72, and from 1.20 to 1.04 in 0.0015, 0.15 and 3.0 molal N_2O_5 solutions, respectively, as the temperature was increased from 25 to 350°. In application, the solubilities may be used to define hydrolysis equilibria and to specify phase stable, aqueous homogeneous-reactor fuels. Some acidities at 25° of unsaturated solutions of $UO_2(NO_3)_2$, HNO_3 and H_2O are included.

KRAUS and others(2) determined the solubility of UO_3 hydrates in HNO_3–H_2O at 25° and thus extended the data of COLANI(3) for the solubility of $UO_2(NO_3)_2$ hydrates in the system UO_3–HNO_3–H_2O. The solubility of $UO_2(NO_3)_2$ in H_2O has been determined at temperatures up to 184°.(4) Later, some qualitative information was obtained on the hydrolytic and thermal stability of $UO_2(NO_3)_2$–H_2O and $UO_2(NO_3)_2$–HNO_3–H_2O solutions at somewhat higher temperatures.(5) From this latter work it was shown that stoicheiometric $UO_2(NO_3)_2$ solutions at temperatures between 250 and 400° precipitated hydrated UO_3. The precipitation could have arisen either from the loss of nitrate to the vapour phase or from the phase instability of the stoicheiometric solutions, or from both effects.

In this present investigation the solubility of UO_3 hydrates in HNO_3–H_2O solutions from 10^{-4} to 6 molal in total nitrate was determined at 25° and from 135 to 350° using a direct sampling method. This method eliminated an assumption for loss of nitrate to the vapour phase. The hydrates proposed to be stable at the several temperatures are specified.

EXPERIMENTAL PROCEDURE

Starting materials were $UO_3 \cdot H_2O$, reagent grade HNO_3, and distilled water. The $UO_3 \cdot H_2O$ obtained from Mallinckrodt Chemical Co., was chemically pure with respect to other metallic oxides but contained approximately 2 mole per cent HNO_3. In order to remove this acid and to remove any other anionic impurity which may have been present, the solid was powdered and then placed in a round bottom flask to which was connected a reflux condenser. Water was added to the flask and was refluxed in contact with the solid for a 16 hr period. Fresh water was substituted and the refluxing

---

* This paper is based on work performed at Oak Ridge National Laboratory which is operated by Union Carbide Corporation for The Atomic Energy Commission.

[1] Previous paper in series: "Liquid–Liquid Immiscibility and Critical Phenomena in the Systems UO_3–SO_3–H_2O, UO_3–SO_3–D_2O, and CuO–SO_3–D_2O, 270–430°C." W. L. MARSHALL, E. V. JONES, G. M. HEBERT and F. J. SMITH, *J. Inorg. Nucl. Chem.* **24**, 995 (1962).

[2] C. A. KRAUS, Manhattan District Project Report A-360, Brown University (1942).

[3] A. COLANI, *Bull. Soc. Chem.* (4) **39**, 1243 (1926).

[4] W. L. MARSHALL, J. S. GILL and C. H. SECOY, *J. Amer. Chem. Soc.* **73**, 1867 (1951).

[5] H. F. MCDUFFIE, *Fluid Fuel Reactors*, (Edited by J. A. LANE, H. G. MACPHERSON and F. MASLAN) Chap. 3, p. 94, Study by W. L. MARSHALL, J. S. GILL and C. H. SECOY. Addison-Wesley, Reading, Mass. (1958).

[illegible] non-soluble impurities. Distilled [illegible] was further purified by passing it through a mixture of [illegible] HNO_3–H_2O [illegible] in the hydrogen and hydroxyl form respectively. The water-washed U[illegible] [illegible] together with HNO_3–H_2O solutions was used in the experiments [illegible] 100 [illegible]

The equipment used and general procedures for the experiments at temperatures above 100° were described previously.[7] The direct sampling procedure was used for sampling the liquid phase in equilibrium with solid and saturated vapour; thus an assumption was unnecessary to account for loss of any component to the vapour phase. A 2 ml volume of 30% C.P. H_2O_2, which decomposed at high temperature to produce O_2, was added to all solutions less than 0.1 molal in total nitrate. At higher concentrations nitrate was sufficient to prevent reduction of U(VI) to U(IV). However, in a few comparative experiments 2 ml and 4 ml volumes of 30% H_2O_2 were added to solutions containing concentrations of nitrate as high as 3 molal.

At temperatures of 135° and above, solution–solid equilibria appeared to be reached in less than 3 hr although some runs were made over 5 day periods. Generally, solution-solid mixtures were rocked for 24 hr at each temperature before the solution phases were sampled. For a set of solution–solid mixtures, samples of the solution phases usually were drawn at several temperatures. Within the precision of the data the solubilities were found to be identical upon sampling at either progressively higher or lower temperatures; thus the equilibria were reversible.

Experiments at 25.0 ± 0.3°C were performed by placing powdered $UO_3 \cdot H_2O$ solid in HNO_3–H_2O solutions which were contained in volumetric flasks. Six stoppered flasks, each containing a Teflon-enclosed stirring bar and a solid–liquid mixture, were placed in a constant temperature bath. Magnetic stirrers under the bath provided stirring. After the solid phases were allowed to settle, samples of the clear solutions were removed for analyses after times of equilibration varying from 8 hr to 3 weeks. Equilibrium at this temperature was believed to be attained in less than 2 days.

Uranium (VI) in the solution phase was determined by controlled-potential coulometric titration after fuming down the samples with H_2SO_4 to remove nitrate, and also by gravimetric ignition to U_3O_8. The particular method used depended upon the UO_3 concentration in solution and upon the desire to confirm analyses using different procedures. Analyses for uranium were made in duplicate and usually agreed within 0.5–1 per cent. Nitrate in solution was determined by titration of HNO_3 after first removing uranium by means of Dowex-50 cation exchanger. At concentrations of nitrate below about 0.01 molal the molal ratio, defined as $m_{UO_3}/m_{N_2O_5} = R_1$, was determined by a method of successive approximation involving the measurement of pH of a sample before and after removal of uranium.[5] Experimentally determined pH data used in this method are given in Table 1. Upon plotting pH against excess $HNO_3 = 2(m_{N_2O_5} - m_{UO_3})$ and using the resultant curves, only one approximation was needed to give a value for excess HNO_3 consistent with the precision of the pH data. Acid–base titrations for total HNO_3 were precise to ±0.4 per cent whereas the direct measurements of pH were precise to ±1 per cent.

The analytical values were obtained in molar units. In order to convert these to molal units, the density of a stoichiometric $UO_2(NO_3)_2$ solution containing the same concentration of UO_3 as the sample solution was assumed to represent approximately the density of the sample solution and was used to make the conversion. This method of estimation was considered valid because

(1) the densities of stoichiometric and those of a few sample solutions experimentally determined showed a first order dependence on UO_3 concentration,
(2) the correction would be large only at concentrations of UO_3 greater than 1 molar where all sample solutions approached stoichiometric $UO_2(NO_3)_2$,
(3) the change in R_1 with moderately large changes in concentration of N_2O_5 was small, and
(4) R_1 is not changed in value upon converting from molar to molal units.

Solid phases were obtained for identification not only by cooling the pressure vessels containing solution and solid phases in the manner described previously[6] but also by cooling vessels containing eight sealed Pyrex tubes which in turn contained $UO_2(NO_3)_2$ solutions and UO_3-hydrate solids. This latter procedure was a modification of the method used for separating two liquid phases.[9] The solid phases were identified by comparison of X-ray diffraction patterns with those reported elsewhere.[10] From the runs using the Pyrex tubes as containers, uranyl silicate trihydrate[11] was also identified. The X-ray diffraction pattern for the silicate was found to be displaced by approximately −0.08 *d* values and agreed with the pattern found by Dawson *et al.*,[10] for the silicate preliminarily identified by them as "phase *III* hydrate."

---

[6] W. L. Marshall and J. S. Gill, *J. Inorg. Nucl. Chem.* **22**, 115 (1961).
[7] J. S. Gill and W. L. Marshall, *Rev. Sci. Instrum.*, **32**, 1060 (1961).
[8] W. L. Marshall, R. Slusher and J. S. Gill, *J. Inorg. Nucl. Chem.* **24**, 889 (1962).
[9] E. V. Jones and W. L. Marshall, *J. Inorg. Nucl. Chem.* **23**, 287 (1961).
[10] J. K. Dawson, E. Wait, K. Alcock and D. R. Chilton, *J. Chem. Soc.* 3531 (1956).
[11] W. L. Marshall and J. S. Gill, *J. Amer. Chem. Soc.* **79**, 1300 (1957).

TABLE 1 THE ACIDITY AT 25°C OF UNSATURATED SOLUTIONS OF $UO_2(NO_3)_2$–HNO_3 AND H_2O
($R_1 = m_{UO_3}/m_{N_2O_5}$, M = Molality)

N_2O_5, (M)	pH	N_2O_5, (M)	pH
R_1 = 0		R_1 = 0.598	
0.2500	0.40	0.2511	0.70
0.1249	0.70	0.1255	1.05
0.0625	1.00	0.0502	1.45
0.03123	1.30	0.02511	1.73
0.01561	1.60	0.00502	2.43
0.00781	1.90	0.002511	2.71
0.003904	2.20	0.000502	3.42
0.001952	2.50		
0.000975	2.80	R_1 = 0.790	
0.000488	3.09	0.2530	1.02
0.0002438	3.37	0.1265	1.35
0.0001219	3.75	0.0506	1.80
		0.02530	2.10
R_1 = 0.396		0.00506	2.75
0.2529	0.50	0.002530	3.10
0.1264	0.92	0.000506	3.70
0.0506	1.28		
0.01264	1.58	R_1 = 0.996	
0.00506	2.23	0.0502	2.80
0.001264	2.50	0.02510	3.02
0.000506	3.20	0.00502	3.45
		0.002510	3.60
		0.000502	4.02

RESULTS AND DISCUSSION

The experimental data for the solubility of UO_3 hydrates in HNO_3–H_2O solutions at temperatures from 25 to 350°C are shown in Fig. 1 plotted as R_1 against the molality of N_2O_5. The scales on the abscissa are displaced for each isotherm. Values of R_1 obtained from preliminary curves drawn through the data were plotted against temperature at several fixed concentrations of N_2O_5. For each of these concentrations curves were drawn through the values. These curves made R_1 self-consistent with temperature usually to better than ±1 per cent and in many cases to ±0.5 per cent although the scatter of experimental data at each temperature was considerably greater. The smoothed values of R_1, derived from these plots and given in Table 2 were used to draw the final curves shown in Fig. 1. The data of KRAUS[(2)] at 25° are included in the figure for comparison. He specified a transition occurring near 0.35 molal N_2O_5 from a $UO_3 \cdot xH_2O$ at lower concentrations to a $UO_3 \cdot yH_2O$.

Since samples were taken at several temperatures during one run the solid phases could only be identified after the last temperature of the operation. Therefore all solution phase samples did not have corresponding identifications of solid phases. Those for which identification of solids was made showed $\alpha UO_3 \cdot H_2O$ as the stable phase at 135, 170 and 200° and $UO_3 \cdot \frac{1}{2}H_2O$ at 300, 325 and 350°. Results at 235 and [illegible] were ambiguous, showing both α and $\beta UO_3 \cdot H_2O$ in many experiments but some[illegible] showing only $\beta UO_3 \cdot H_2O$. Results given in Table 3 of separate runs in Pyrex

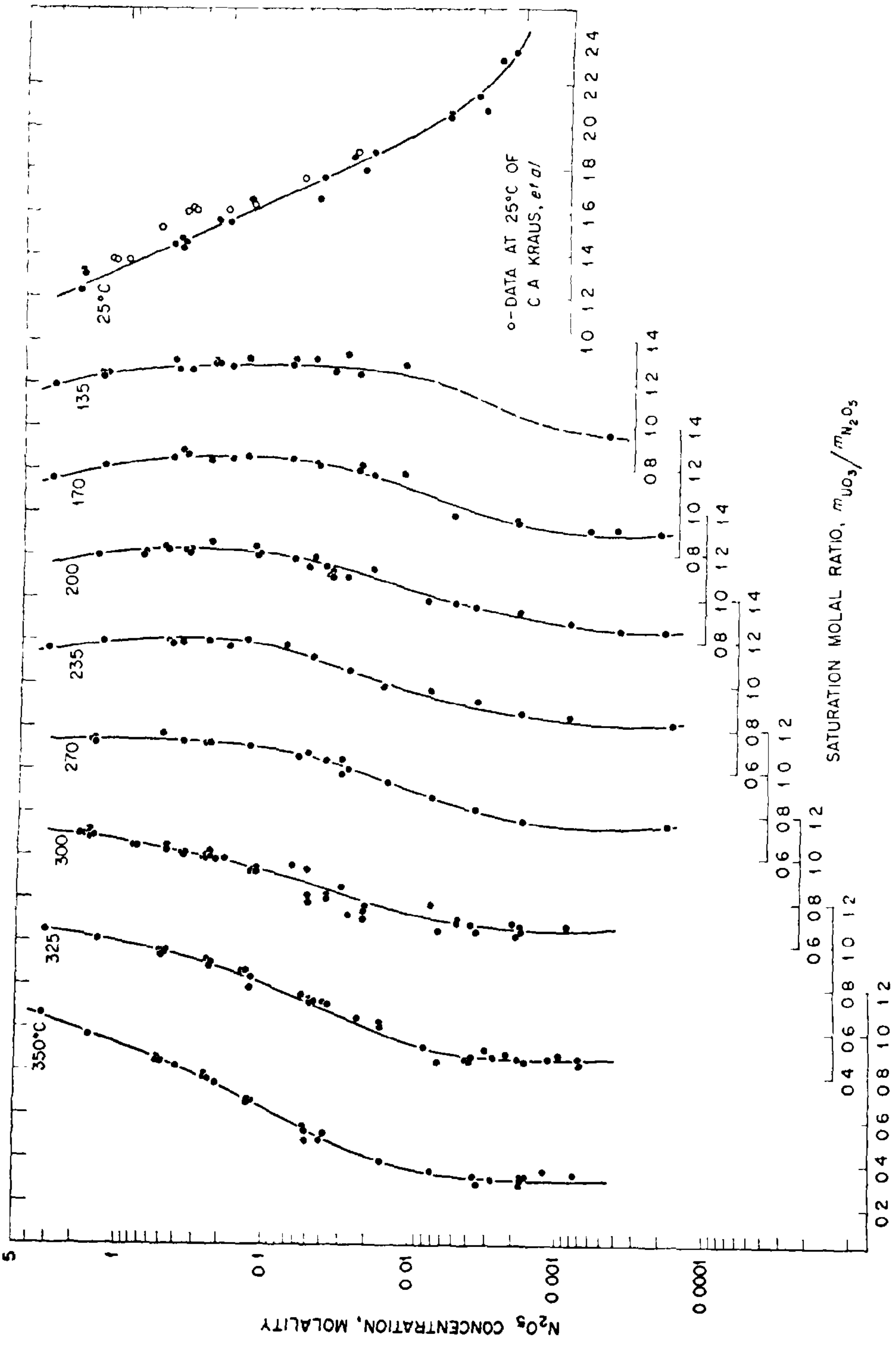


FIG. 1.—The solubility of UO_3 hydrates in HNO_3-H_2O solutions, 25–350°C.

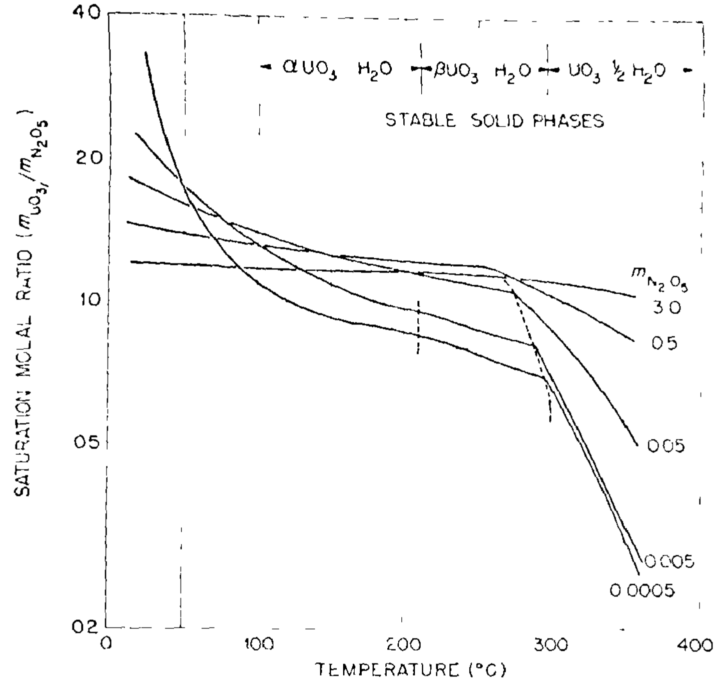


FIG. 2. The saturation molal ratio, R_t, as a function of temperature, system UO_3–N_2O_5–H_2O.

TABLE 2. SMOOTHED VALUES FOR THE SOLUBILITY OF UO_3 HYDRATES IN HNO_3–H_2O SOLUTIONS, 25–350°C, 0.0005–3.0 MOLAL N_2O_5

t (°C)	$m_{N_2O_5}$ (molality) Solid phase	3.00	1.500	0.500	0.1500	0.0500	0.01500	0.00500	0.001500	0.000500
						R_t *				
25	$\alpha UO_3\cdot H_2O$	1.200	1.290	1.440	1.600	1.750	1.910	2.120	2.600	~3.20†
135	$\alpha UO_3\cdot H_2O$	1.176	1.228	1.280	1.290	1.280	1.248	1.150†	1.018†	0.952†
170	$\alpha UO_3\cdot H_2O$	1.170	1.208	1.250	1.256	1.220	1.146	1.034	0.948	0.900
200	$\alpha UO_3\cdot H_2O$	1.162	1.196	1.230	1.226	1.170	1.070	0.974	0.910	0.864
235	$\beta UO_3\cdot H_2O$	1.154	1.186	1.212	1.184	1.118	1.004	0.910	0.856	0.814
270	$\beta UO_3\cdot H_2O$	1.132	1.146	1.142	1.120	1.064	0.950	0.842	0.764	0.746
300	$UO_3\cdot \frac{1}{2}H_2O$	1.110	1.086	1.046	0.976	0.884	0.776	0.700	0.670	0.664
325	$UO_3\cdot \frac{1}{2}H_2O$	1.080	1.040	0.958	0.850	0.720	0.582	0.490	0.470	0.470
350	$UO_3\cdot \frac{1}{2}H_2O$	1.048	0.980	0.860	0.714	0.550	0.414	0.334	0.322	0.318

* $R_t = m_{UO_3}/m_{N_2O_5}$
† Estimated

tubes at concentrations of N_2O_5 varying from 0 to 1.5 molal showed the existence of $\alpha UO_3\cdot H_2O$ as the stable phase at 25, 135, 170 and 200°, $\beta UO_3\cdot H_2O$ at 235 and 270 nd $UO_3\cdot \frac{1}{2}H_2O$ at 300 and 325°. The transition at 25° specified by KRAUS and determined by the Schreinemaker's method, was not revealed. In his investigation solution nd solid mixtures were equilibrated for 24–48 hr before analyses of both phases us the times of equilibration were comparable with those in this study. The two lids $\alpha UO_3\cdot H_2O$ and $\beta UO_3\cdot H_2O$ identified at 270° showed that complete equilibrium r 17 hr with respect to solid phases was not yet established. After the longer ths of time only $\beta UO_3\cdot H_2O$ was identified in agreement with expectations. At however, after 72 hr $\alpha UO_3\cdot H_2O$ in addition to $\beta UO_3\cdot H_2O$ was still found. The

TABLE 3. — IDENTIFICATION OF SOLID PHASES AFTER EQUILIBRATION WITH HNO_3–H_2O SOLUTIONS IN PYREX TUBES

T (°C)	Time (hr)	Solid phases†		
25	144	A		
135	72	A		
170	72	A		
200	72	A		
235	72	A	B	S
270	17	A	B	S
270	48		B	S
270	91		B	S
300	48		C	S
325	48		C	S

Runs at designated temperatures with solutions 0, 0.00015, 0.005, 0.015, 0.15, 0.5 and 1.5 molal in N_2O_5.

† A = $\alpha UO_3 \cdot H_2O$; B = $\beta UO_3 \cdot H_2O$; C = $UO_3 \cdot \frac{1}{2}H_2O$; S = $(UO_2)_2SiO_4 \cdot 3H_2O$.

solid $(UO_2)_2SiO_4 \cdot 3H_2O$ listed in Table 3 was formed by reaction of UO_3 hydrate with the Pyrex glass. In many of the experiments at concentrations of N_2O_5 above 1 molal, UO_3 hydrate had been consumed completely by this reaction.

In liquid water in the presence of vapour, a transition from $\alpha UO_3 \cdot H_2O$ to $\beta UO_3 \cdot H_2O$ was reported to occur at about 205°,[12] while that for $\beta UO_3 \cdot H_2O$ (designated orthorhombic II phase in Reference 10) to $UO_3 \cdot \frac{1}{2}H_2O$ was found between 280 and 320°C.[10] At 270°, upon evaluation of the overall symmetry of the solubility curves R_t vs. log $m_{N_2O_5}$ both with temperature and concentration, $\beta UO_3 \cdot H_2O$ would appear to be the stable solid in contact with solutions up to 0.05 molal N_2O_5 and $UO_3 \cdot \frac{1}{2}H_2O$ at higher concentrations. Values of R_t obtained from the smoothed data (Table 2) and plotted against temperature at fixed concentrations of N_2O_5 (Fig. 2) show this transition from $\beta UO_3 \cdot H_2O$ to $UO_3 \cdot \frac{1}{2}H_2O$ as sharp breaks in the solubility curves. Identification of the solid phases at 270° (Table 3), nevertheless, showed only $\beta UO_3 \cdot H_2O$ as the stable solid at all concentrations of N_2O_5 investigated. Regardless of this uncertainty at 270°, there still seems to be a strong dependence of the transition temperature upon N_2O_5 concentration. In the presence of both solution and its saturated vapor the transition will occur at the temperature where the vapour pressure (p) of the hydrate becomes greater than that of H_2O in the solution phase. In Fig. 3 the point A is estimated for the transition from $\beta UO_3 \cdot H_2O$ to $UO_3 \cdot \frac{1}{2}H_2O$ in liquid H_2O in equilibrium with its vapour phase, and point B for the transition in 0.3 molal $UO_2(NO_3)_2$ solution where the vapour-pressure is estimated roughly to be $p_{soln} = N_1 p_0$ (N_1 = mole fraction of H_2O in the $UO_2(NO_3)_2$ solution, p_0 = vapour-pressure of H_2O). At these points the vapour-pressure of H_2O for the three phase equilibrium, $\beta UO_3 \cdot H_2O$ – $UO_3 \cdot \frac{1}{2}H_2O$ – $\frac{1}{2}H_2O$, in the condensed system equals that of the liquid phase. Fig. 3 shows that the slope, $d(\log p)/d(1/T)$, for the equilibrium is near that for the equilibrium $(H_2O)_{liq} = (H_2O)_{vap}$, thus ΔH derived from the slope for the reaction $UO_3 \cdot H_2O \rightarrow UO_3 \cdot \frac{1}{2}H_2O + \frac{1}{2}H_2O$ probably is near +9 kcal/mole.

---

[12] W. L. MARSHALL, *Analyt. Chem.* **27**, 1923 (1955).

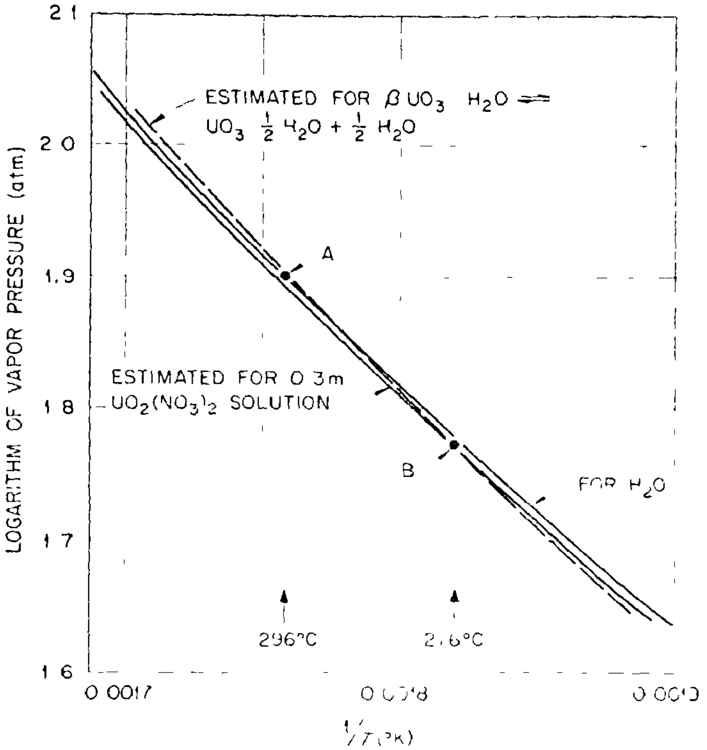


FIG. 3. Estimated log vapour pressure vs $1/T$(°K) for the three-phase equilibrium $\beta UO_3 \cdot H_2O \rightleftharpoons UO_3 \cdot \frac{1}{2}H_2O + \frac{1}{2}H_2O$.

In the studies above 100° a saturated vapour-phase consisting of varying amounts of HNO_3 and nitrogen oxides in addition to water was always present and was especially evident at the higher temperatures. Solutions of $UO_2(NO_3)_2$ from 0.5 to 2

TABLE 4. SOLUBILITY OF $UO_3 \cdot \frac{1}{2}H_2O$ IN HNO_3–H_2O AT 300°C IN THE PRESENCE AND ABSENCE OF ADDED O_2

H_2O_2* Added (ml)	N_2O_5 (m)	R_U†	(m/M)‡ at 25°C
4.0	1.604	1.098	1.154
2.0	1.786	1.098	1.173
0	1.981	1.102	1.194
4.0	0.2319	0.992	1.024
2.0	0.2550	0.992	1.026
0	0.2854	0.994	1.028
4.0	0.0217	0.778	1.005
2.0	0.0276	0.738	1.005

* Added to 25 ml of liquid phase, decomposes to H_2O–O_2 at high temperature.
† $m_{UO_3}/m_{N_2O_5}$ after 24 hours at 300°C.
‡ m = molality, M = molarity.

al in concentration were observed in sealed silica capillary tubes at temperatures een 250 and 350°. The vapour-phases within the tubes rapidly became coloured increasing the temperature. The colour varied from a light yellow at 250° to a dark red (almost opaque) at 350 At the higher temperatures a slightly red coloration was observed in the liquid phase and was considered to be caused by dissolved NO_2 or N_2O_4 Upon cooling the solutions to room temperature by inserting a tube under water the coloration in both the vapour and liquid phases disappeared within a few seconds the time required to cool—thus indicating rapid reversibility of these equilibria If the presence of *nitrogen oxides* in particular NO in the liquid phase affected the solubilities of UO_3 hydrates then an excess of O_2 added to the container might be expected to lower the concentration of NO by the reaction, $2NO + O_2 \rightarrow 2NO_2$, and thus give different solubilities In testing this proposition, the results given in Table 4 showed no detectable effect of oxygen at least for the amounts added

At a fixed concentration of N_2O_5 the solubilities of UO_3 hydrates decrease with temperature in the same manner as in solutions containing SO_3 and H_2O (6) The large decrease in R_1 with temperature above 300 may not only be the result of the transition of $\beta UO_3 \, H_2O$ to $UO_3 \, \frac{1}{2}H_2O$ but also the result of the large decrease in dielectric constant of the solvent and corresponding decrease in acidity of nitric acid

J Inorg Nucl Chem 1963 Vol 25 pp 291 to 301 Pergamon Press Ltd Printed in Northern Ireland

THE EXTRACTION OF LITHIUM CHLORIDE BY TRI-N-BUTYL PHOSPHATE

D F C Morris and E L Short
Department of Chemistry, Brunel College, London W 3

(*Received* 23 *May* 1962, *in revised form* 23 *July* 1962)

Abstract— The extraction of lithium chloride from aqueous solutions by tri-n-butyl phosphate (TBP) has been investigated. Lithium chloride in the organic phase behaves as an associated electrolyte with a dissociation constant $\sim 5 \times 10^{-6}$. It has been shown that up to ca 0.96 M LiCl in the organic phase there is no strong TBP salt interaction but there appears to be a definite tendency for the extracted lithium chloride to possess a primary hydration number of four. At higher concentrations TBP molecules begin to substitute for H_2O molecules in the solvation shell of the extracted LiCl but a total solvation number of four seems to be maintained. Physical properties suggest the possibility of aggregation in the most concentrated extracts.

Baldwin *et al*⁽¹⁾ and Healy and Brown⁽²⁾ have studied the extraction of lithium chloride by tri-n-butyl phosphate (TBP). The present paper contains new results for the system and our investigation in many ways parallels the examination of the system TBP–HCl–H_2O by Kertes⁽³⁾

EXPERIMENTAL

Reagents A concentrated solution of laboratory grade lithium chloride was purified by filtration and by passage through a column of the anion-exchange resin Deacidite-FF in the Cl -form. Calculated amounts of the solution were taken for the preparation of a number of stock solutions of various concentrations. These were standardized by Volhard's method involving the addition of a little nitrobenzene. TBP was purified by the method of Alcock *et al*⁽⁴⁾ The dried compound was finally distilled under reduced pressure (b p 142 at 2 3 mm pressure). Benzene used in some experiments was material from BDH 'for molecular weight determinations'.

Equilibrium and volume change measurements The swelling of the organic phase due to transfer of aqueous lithium chloride was measured in 10 ml graduated (0.1 ml) centrifuge tubes; these had been thoroughly cleaned to ensure a complete separation of the phases. Five ml of pure TBP were carefully added from a 10 ml microburette to 5 ml of standardized lithium chloride solution. The positions of the liquid–liquid interface and of the liquid–air meniscus were immediately noted. In each case the stoppered tube was then shaken mechanically for 15 min. After centrifuging the positions of the menisci were read to within 0.025 ml. The average was taken of two determinations for each standard solution of lithium chloride. The ambient temperature was 20 ± 1 during these measurements.

Measurements of the distribution of lithium chloride Two ml aliquots of each layer in the tubes from the equilibrium measurements were separated by means of transfer pipettes. Each aliquot (after dilution where necessary) was analysed for chloride content by the Volhard method. All analyses were preformed in duplicate. The estimated total chloride content of both organic and aqueous phases after equilibration always corresponded with the initial total chloride to within 2 per cent.

Measurements of density A pyknometer, calibrated according to specification ASTM D 941 was used to determine the densities of the freshly equilibrated organic layers at 20 ± 0.1. The values of density obtained were used in the calculation of values of the viscosity in centipoises.

Measurements of viscosity The viscosities of the organic phases were determined by means of an Ubbelhode (suspended level) No 1 viscometer (B S S 188) at 20 ± 0.1. The viscometer was calibrated by use of a 40 per cent sucrose solution. The time of flow between calibration marks was measured to within 0.1 sec with a stop-watch.

Measurements of conductivity Resistance measurements were carried out using a bridge network,

---

W H Baldwin, C E Higgins and B A Soldano *J Phys Chem* **63**, 118 (1959)

T V Healy and P F Brown Report, AERE C/R 1970 (1956)

A S Kertes, *J Inorg Nucl Chem* **14**, 104 (1960)

K Alcock, S S Grimley, T V Healy, J Kennedy and H A C McKay, *Trans Faraday Soc* 52, 39 (1956) oscillator and amplifier similar to those described by DIPPY and HUGHES.[5] A six decade resistance box (max. resistance 111 111 Ω) was used in series with a single decade megohm box. The capped conductivity cell was constructed of Pyrex glass and had a capacity of ca. 10 ml. The stout, greyed-platinum electrodes were mounted rigidly by means of small Pyrex struts at a distance of 2 mm apart. No solvent correction was necessary, since the conductance of TBP phases was due solely to extracted hydrated electrolyte. The cell constant was determined by use of a standard solution of potassium chloride as described by DIPPY *et al.*[6] All measurements were carried out in a thermostatic water bath at 20 ± 0.02°.

Water determinations. The water content of the TBP layers was found by means of the Karl Fischer reagent, using the dead-stop endpoint method as determined with a Fischer Titrimeter. The reagent was standardized against a known (Fischer Scientific Reagents) solution of water in methanol. In addition, the reagent was checked by titration against TBP equilibrated with water.

Measurements of refractive index. Refractive indices for the sodium *D* doublet were measured using an Abbe refractometer. All measurements were performed at 20 ± 1°.

Measurements with TBP diluted with benzene. Some experiments were performed with solutions of TBP in benzene as the organic phase. In these cases the lithium chloride content of an equilibrium organic layer was determined using an EEL flame photometer, the salt being washed into water before measurement.

Degradation of TBP. It has been shown by various workers[7-10] that aqueous solutions of chlorides can promote decomposition of TBP. To investigate the possibility of degradation of TBP by aqueous lithium chloride, potentiometric, gas chromatographic, density and viscosity measurements were performed on organic phases at various times after equilibration. Potentiometric titrations were carried out using an EIL direct reading pH-meter, model 23A. A very high sensitivity 40ft-nylon capillary Argon Chromatograph loaded with a thin film of dinonyl phthalate and with a micro Lovelock detector was used to detect and determine more volatile decomposition products.

RESULTS

To permit a ready comparison to be made between properties of the systems TBP–LiCl–H_2O and TBP–HCl–H_2O, results are presented in a similar manner to that employed by KERTES.[8]

Partition of the lithium chloride

The molar concentrations of lithium chloride in the initial aqueous solutions and in both the equilibrium organic and aqueous layers are listed in Table 1. Column (6) shows the calculated distribution coefficients, *D*, where

$$D = [\mathrm{LiCl}]_0/[\mathrm{LiCl}]$$

In column (7) are given the calculated mass distribution coefficients, μ, where

$$\mu = \frac{\text{total amount of LiCl in the organic layer}}{\text{total amount of LiCl in the aqueous layer}}$$

The relationship between the two distribution ratios is given by

$$\mu = \frac{V_0}{V} D$$

where V_0 and V represent the volumes of the equilibrium organic and equilibrium aqueous layers, respectively. The increases in volume of the organic phases are given in column (5) of Table 1, and values of the ratio V_0/V are listed in Table 2, column (3).

---

(5) J. F. J. DIPPY and S. R. C. HUGHES, *J. Chem. Soc.* 953 (1954).

(6) J. F. J. DIPPY, S. R. C. HUGHES and J. W. LAXTON, *J. Chem. Soc.*, 1470 (1954).

(7) A. J. MOFFAT and R. D. THOMPSON, *J. Inorg. Nucl. Chem.* **16**, 363 (1961).

(8) A. S. KERTES and M. HALPERN, *J. Inorg. Nucl. Chem.* **20**, 117 (1961).

(9) A. S. KERTES and M. HALPERN, *J. Inorg. Nucl. Chem.* **16**, 308 (1961).

(10) A. S. KERTES and M. HALPERN, *J. Inorg. Nucl. Chem.* **19**, 359 (1961).

TABLE 1

No of soln	Molarity of LiCl: In the initial aqueous soln [LiCl]	Molarity of LiCl: In the equil aqueous phase [LiCl]	Molarity of LiCl: In the equil organic phase $[LiCl]_o$	Vol increase of the organic phase (ml)	D	μ	LiCl in the organic phase, mmole*	LiCl/TBP ratio	H_2O in the organic phase, mmole*	H_2O/TBP ratio
1	2	3	4	5	6	7	8	9	10	11
1	0.4796	0.5084	0.001	0.30	0.002	0.002	0.005	0.0003	18.2	0.99
2	0.9734	1.040	0.002	0.30	0.002	0.002	0.011	0.0006	18.5	1.01
3	1.463	1.545	0.004	0.30	0.003	0.003	0.021	0.0012	18.1	0.99
4	1.952	2.060	0.005	0.30	0.002	0.003	0.027	0.0015	18.1	0.99
5	2.412	2.556	0.008	0.30	0.003	0.004	0.042	0.0023	15.7	0.86
6	2.942	3.005	0.014	0.275	0.0047	0.005	0.074	0.0040	14.8	0.81
7	3.330	3.490	0.0195	0.275	0.0056	0.006	0.103	0.0056	14.7	0.80
8	3.773	3.995	0.0240	0.275	0.0060	0.007	0.127	0.0069	13.3	0.73
9	4.723	4.919	0.0555	0.25	0.0113	0.013	0.291	0.0159	12.2	0.67
10	5.230	5.432	0.0770	0.20	0.0142	0.015	0.400	0.0219	11.2	0.61
11	5.751	5.911	0.1089	0.15	0.0184	0.020	0.561	0.0306	10.5	0.57
12	6.235	6.329	0.1599	0.15	0.0253	0.027	0.824	0.0450	9.7	0.53
13	6.578	6.665	0.1960	0.125	0.0294	0.031	1.005	0.0549	10.8	0.59
14	6.993	7.094	0.3049	0.175	0.0430	0.046	1.578	0.0862	11.4	0.62
15	7.590	7.460	0.4433	0.225	0.0612	0.066	2.305	0.1260	13.2	0.72
16	8.290	8.100	0.6811	0.30	0.0841	0.095	3.610	0.1973	16.2	0.89
17	9.186	8.775	0.9577	0.375	0.1091	0.127	5.148	0.2813	19.7	1.08
18	10.05	9.783	1.0987	0.475	0.1123	0.136	6.015	0.3287	22.5	1.23
19	11.14	10.95	1.298	0.50	0.1185	0.145	7.139	0.3901	23.0	1.26
20	12.24	11.67	1.530	0.50	0.1509	0.184	8.950	0.5296	22.6	1.23
21	13.40	12.77	1.836	0.50	0.1560	1.190	10.098	0.5518	22.6	1.23

* The number of mmoles of a substance extracted is the number of mmoles present in the whole organic phase at equilibrium resulting from the agitation of 5 ml of TBP with 5 ml of aqueous solution

TABLE 2

No of soln	ρ Density at 20 (g/cm³)	Ratio I_0/I of the equilib phases	n_D 20 Refractive index	η Viscosity at 20 (centipoise)	$10^3\kappa$ Specific conductance at 20 (Ω^{-1} cm^{-1})	Λ Equivalent conductance at 20 (Ω^{-1} cm^{2})	α Degree of dissociation
1	2	3	4	5	6	7	8
1	0.9799	1.13	1.419	4.687	0.0720	0.7294	0.057
2	0.9793	1.13	1.419	4.603	0.1245	0.6223	0.048
3	0.9839	1.13	1.419	4.972	0.1727	0.4319	0.036
4	0.9837	1.13	1.419	4.975	0.2138	0.4275	0.035
5	0.9839	1.13	1.419	4.910	0.2468	0.3085	0.025
6	0.9839	1.12	1.419	4.956	0.3024	0.2160	0.018
7	0.9841	1.12	1.419	4.930	0.2962	0.1519	0.013
8	0.9841	1.12	1.419	4.952	0.3878	0.1616	0.013
9	0.9843	1.11	1.419	5.043	0.4643	0.0837	0.0070
10	0.9843	1.08	1.421	5.156	0.5595	0.0727	0.0062
11	0.9860	1.06	1.422	5.327	0.6622	0.0608	0.0054
12	0.9871	1.06	1.422	5.735	0.8686	0.0543	0.0031
13	0.9895	1.05	1.422	6.241	1.3072	0.0667	0.0069
14	0.9918	1.07	1.423	7.108	1.5157	0.0497	0.0059
15	0.9951	1.09	1.426	8.723	1.6606	0.0374	0.0054
16	1.003	1.13	1.427	13.22	2.3188	0.0341	0.0075
17	1.011	1.16	1.428	20.82	2.2914	0.0239	0.0083
18	1.018	1.21	1.429	34.04	2.1594	0.0197	0.011
19	1.025	1.22	1.430	51.54	1.6928	0.0130	0.011
20	1.030	1.22	1.431	89.87	1.2329	0.0081	0.0217
21	1.034	1.22	1.432	127.24	0.8450	0.0046	0.059

The concentrations of lithium chloride in the equilibrium organic and aqueous phases are plotted in Fig 1 The distribution isotherm indicates that the extraction of lithium chloride from water into TBP is not uniform The break in the curve corresponds with that in Fig 2 in which the percentage of lithium chloride extracted is plotted against the concentration of the initial aqueous solutions

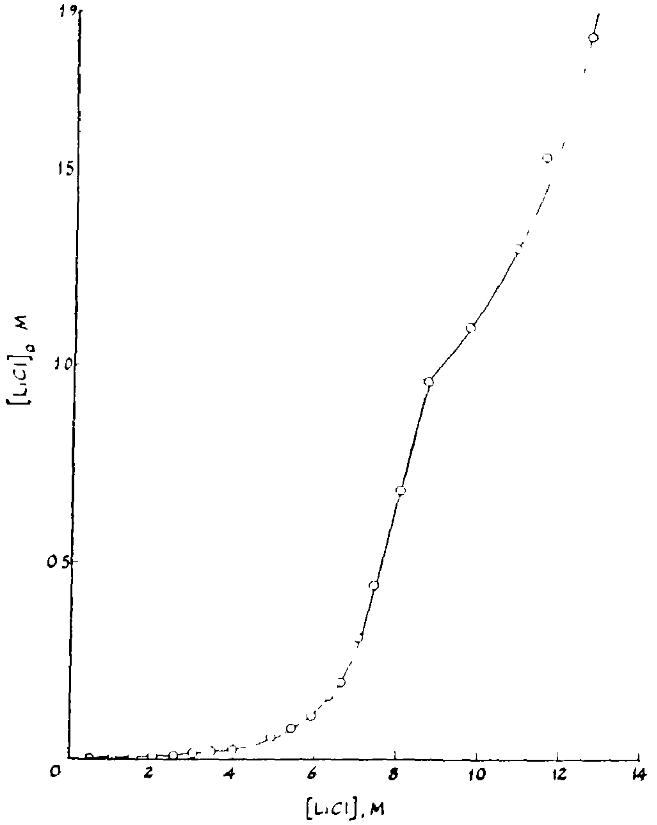


Fig 1 – Concentration of lithium chloride in the equilibrium organic phase against concentration in the equilibrium aqueous phase

Swelling of the TBP *phase* The volume increases of the organic phases in ml are plotted against mmoles of lithium chloride extracted in Fig 3 Three breaks in the curve are clearly distinguishable A plot of the ratio V_0/V against mmoles of LiCl extracted shows three breaks at corresponding positions

Density of the TBP *phase* Experimental values for the densities of the organic phase at equilibrium are quoted in column 2 of Table 2 These results are plotted against the amount of lithium chloride extracted in Fig 4 The curve shows two breaks which correspond with breaks in the previous plots

Viscosity of the TBP *phase* The viscosities in centipoises of the series of organic extracts are tabulated in column (5) of Table 2 The plot of η against mmoles of LiCl extracted (Fig 5) shows one intersection corresponding to 5 1 mmole of LiCl in the organic phase

Conductivity of the TBP *phase* The measured specific conductances and the equivalent conductances of the equilibrium organic phases are listed in columns (6) and (7)

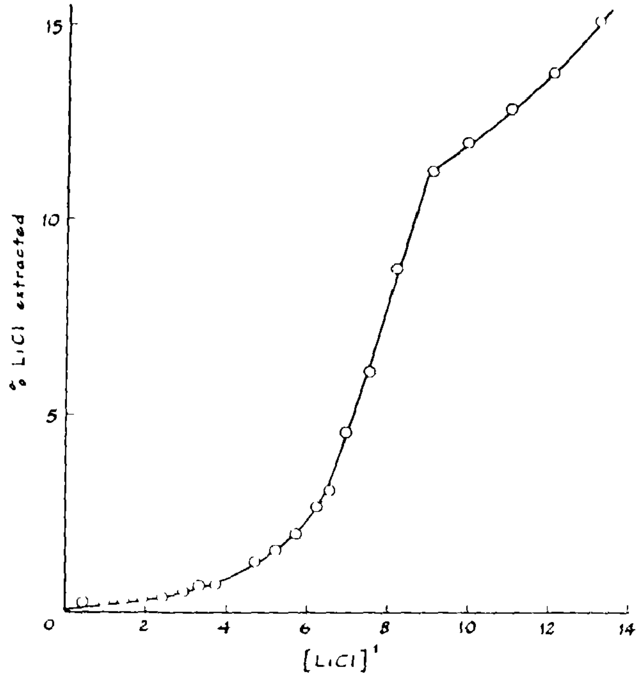


FIG. 2 Dependence of percentage of lithium chloride extracted on molarity of the initial aqueous solution

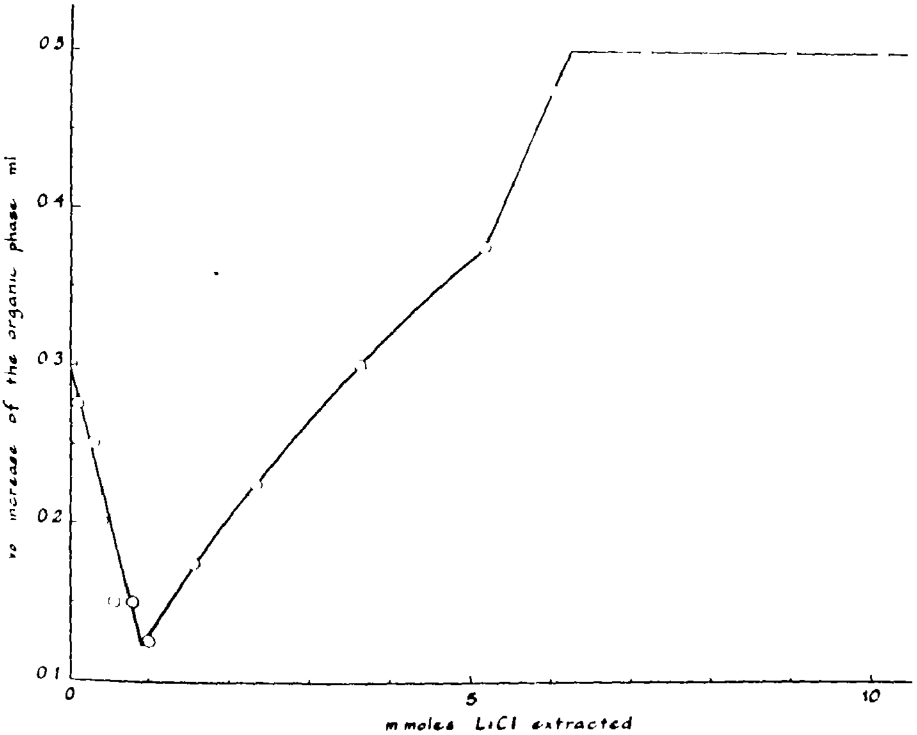


FIG. 3—Increase in volume of the organic phase corresponding to amount of LiCl extracted

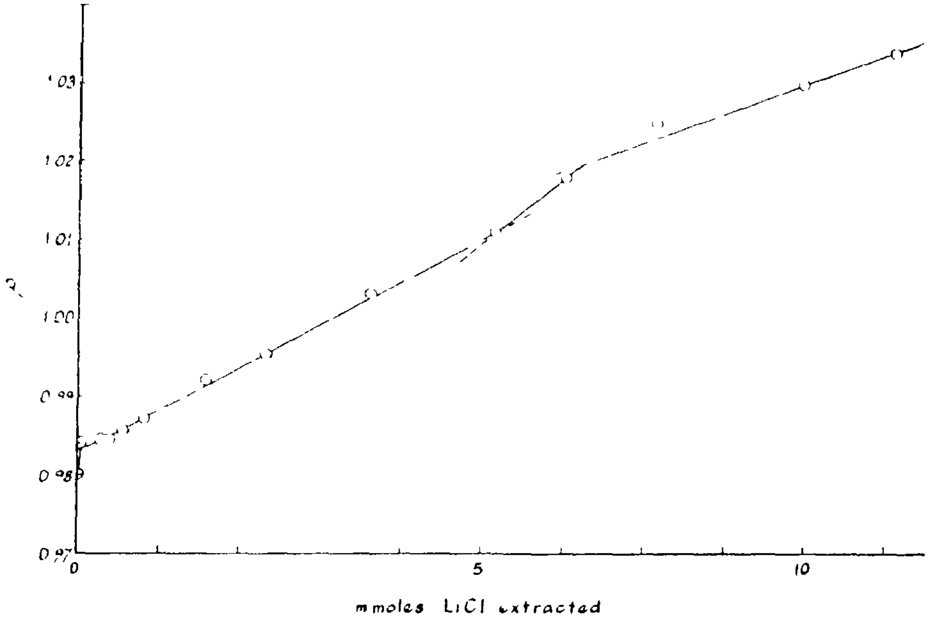


FIG. 4 Density of the equilibrium organic phase versus mmole of LiCl extracted

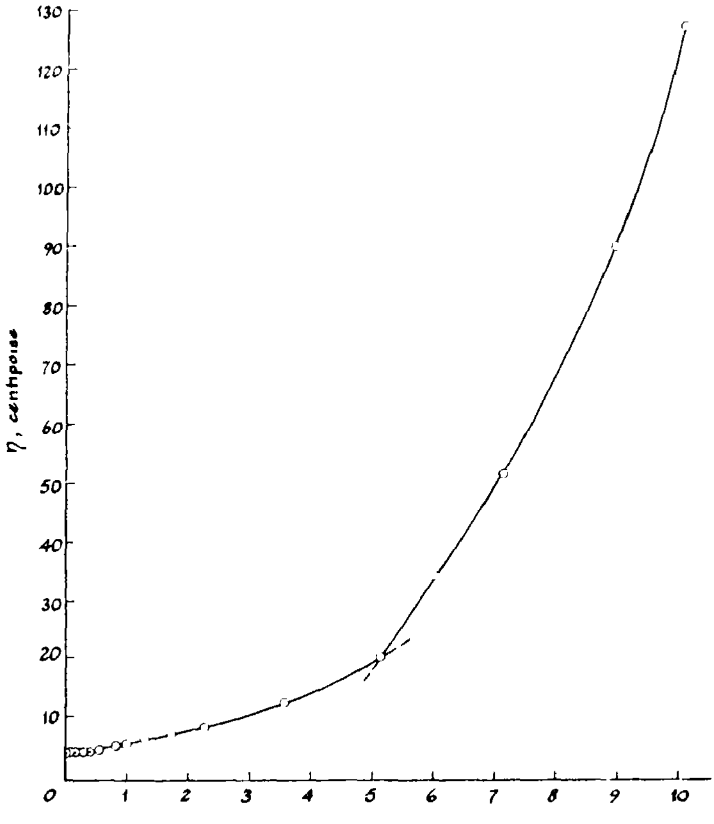


FIG. 5 —Viscosity of the equilibrium organic phase against mmole of LiCl extracted

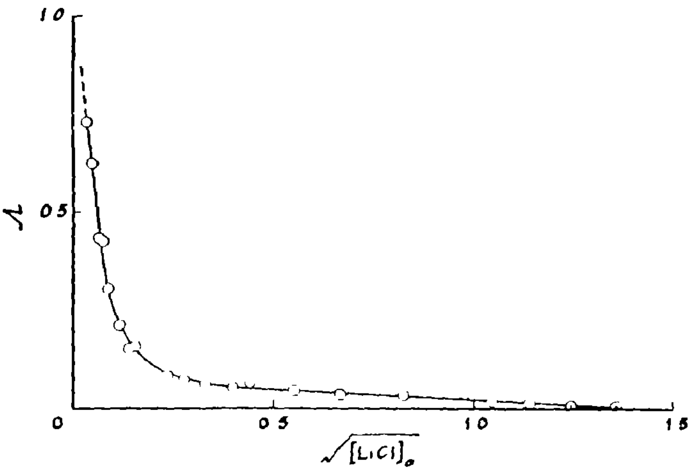


FIG. 6 — Equivalent conductance of lithium chloride in the equilibrium organic phases

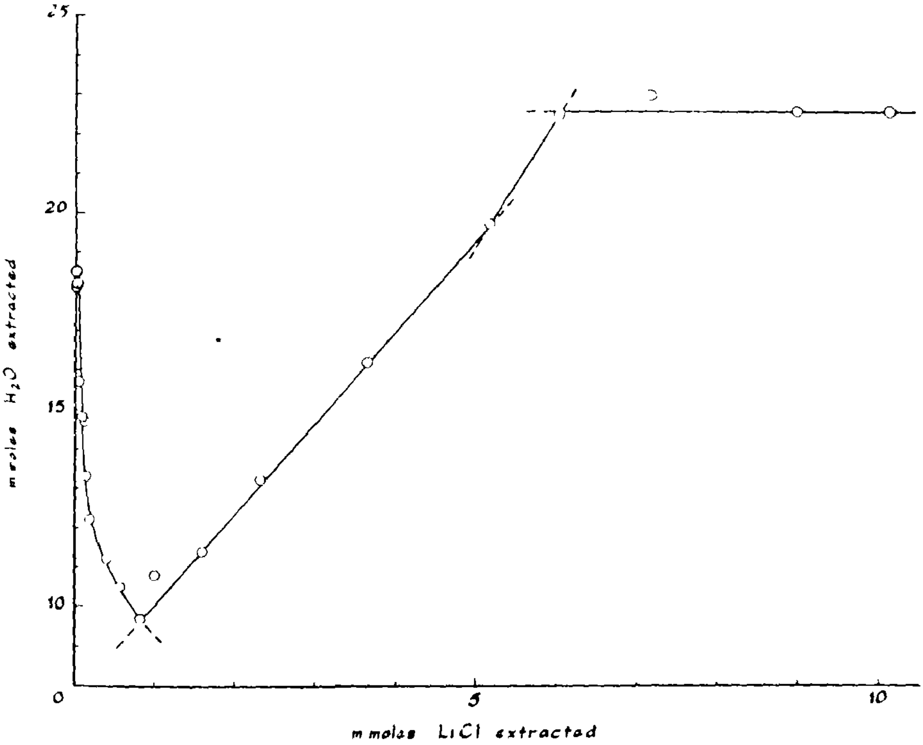


FIG. 7 — H_2O extracted into the organic phase against LiCl extracted

of Table 2 Fig 6 shows a Kohlrausch plot of conductivity data The form of the curve is typical for solutions of an associated electrolyte

Water content of the TBP *phase* Numerical data for the water content of the organic phases are given in columns (10) and (11) of Table 1 The results are plotted in Fig 7

TBP saturated with water contains one mole of H_2O per mole of TBP and there appears to be formed a definite TBP monohydrate (1,11) The negative slope of the first part of the curve in Fig 7 can be attributed to the lowering by lithium chloride of the water activity in the aqueous phase leading to a resultant decrease in the partition of (non salt hydrate) water (12) After 0 9 mmole of LiCl have been extracted such an effect appears to be offset by increasing extraction of hydrated salt into the organic layer Following the procedure of YATES *et al* (13) application of Henry's law to water extraction in the region of small lithium chloride extraction yields a constant value for $(a_w)_o/a_w$ of 3 5 (a_w water activity subscript o denotes organic phase)

The slope of the second part of the curve in Fig 7 is 2 3, indicating that each lithium chloride molecule is accompanied by 2 3 water molecules on passing from the aqueous phase into TBP After 5 1 mmoles of LiCl have been extracted there is an increase in the slope of the curve to 3 3, and after 6 1 mmole of LiCl have entered the organic phase further salt is extracted without accompanying water

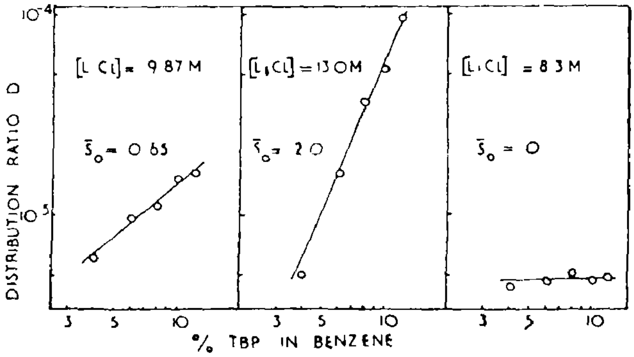


FIG 8 —The extraction of LiCl into TBP diluted with benzene Variation of the distribution ratio with concentration of TBP in the organic phase

Solutions of TBP *in benzene as the organic phase*

To gain information on the average number of molecules $\bar{s}$ of TBP directly associated with extracted LiCl, results of experiments with dilute solutions of TBP in benzene as the organic phase were used For constant aqueous phase conditions and low concentrations of TBP, activity coefficients in the organic phase can be neglected and the limiting law

$$D \propto [\text{TBP}]^{\bar{s}}$$

$$(\partial \log D/\partial \log [\text{TBP}]) = \bar{s}$$

should apply Using this method over the range 1–12 per cent (volume fraction) TBP in benzene, plots on logarithmic scales of D vs per cent TBP in benzene yielded straight lines. These corresponded to values for $\bar{n}$ of 0, 0.65 and 2 for respective values of [LiCl] of 8.30, 9.87 and 13.0 M (Fig. 8).

---

(11) D J TUCK, *J Chem Soc* 2783 (1958)

(12) L I KATZIN and J C SULLIVAN, *J Phys Colloid Chem* **55**, 346 (1951)

(13) P C YATES, R LARAN, R E WILLIAMS and T E MOORE, *J Amer Chem Soc* **75**, 2212 (1953)

Chemical stability of TBP

All the results reported above were obtained within 4 hr of equilibration, except the conductivity results which were determined within eight hours after equilibration. Since it has been shown that TBP is prone to degradation in the presence of aqueous solutions of various chlorides[7–10] the chemical stability of the phosphate under the present experimental conditions was investigated.

Over a period of up to one day after equilibration, potentiometric titrations of organic extracts with standard alkali in a 3 : 1 ethanol : water mixture showed no evidence of hydrolysis which would have led to the formation of butyl phosphoric acids. However, it has been shown[7,8] that the degradation of TBP promoted by hydrochloric acid involves fission of the Bu–O bond rather than true hydrolysis. Our gas chromatographic studies of the vapours of organic extracts showed no butyl chloride over a time of 20 hr after equilibration in the case of organic extracts with $[LiCl]_0$ = 0.002 or 0.15 M. The sensitivity of the procedure was such that 5 × 10^{-3} mmole of butyl chloride could be detected in 5 ml of organic phase. An organic extract with $[LiCl]_0$ = 1.36 M was found to contain 0.01 mmole of butyl chloride 4.5 hr after equilibration and 0.025 mmole of the alkyl chloride 6.5 hr after equilibration. After a period of 19 hr the phase contained 0.04 mmole of butyl chloride; this corresponds to only 0.22 per cent of the original TBP having been converted into dibutyl phosphoric acid.

Maximum variations in densities and viscosities of organic phases at 20° noted over a period of one day after equilibration were as follows:

$[LiCl]_0$ (M)	$\Delta\rho$ (%)	$\Delta\eta$ (%)
0.002	0.01	1.2
0.15	0.03	0.6
1.36	0.01	2.8

The observations reported in this section suggest that decomposition of TBP by lithium chloride and water does not pertinently affect physical chemical measurements on organic phases made within eight hours of equilibration. It is interesting to note that an unstable hydration phenomenon similar to that reported by KERTES[13] was observed in the case of the $[LiCl]_0$ = 1.36 M solution about eight days after equilibration.

DISCUSSION

From the conductivity results an approximate measure of the degree of dissociation α of lithium chloride in the organic layers has been estimated from the formula[14] $\alpha = \Lambda/\Lambda_0$. The calculated values, presented in Table 2, column (8) show that the lithium chloride exists to a large extent as ion-pairs. The Ostwald dilution law explains the results over a considerable range and leads to a dissociation constant of ca. 5 × 10^{-6}

A. S. KERTES, *J. Inorg. Nucl. Chem.* **12**, 377 (1960).

H. A. C. MCKAY and A. R. MATHIESON, *Trans. Faraday Soc.* **47**, 428 (1951).

In many cases of the extraction of salts MX into TBP[(2)] the activity coefficient of MX in the organic phase may be taken as unity for concentrations $[\mathrm{MX}]_0$ up to ca 0.1 M. However, in the present system the expression $(1 - \gamma)\,[\mathrm{LiCl}]_0/\gamma^2 m^2$ is not constant for values of $[\mathrm{LiCl}]_0$ from 10^{-3} to 10^{-1} M (m is the molality of lithium chloride in the equilibrium aqueous phase and γ is the mean activity coefficient of LiCl in aqueous solution). This "abnormal behaviour", which was first pointed out by Healy and Brown, could possibly be due to the fact that lithium chloride is more complexed than other 1:1 salts in either the aqueous or organic phase.[(16)] On the other hand the result is probably due merely to changes in the activity coefficient of lithium chloride in the organic layer as a result of the wide variation in water content of the TBP phases.

For concentrations of lithium chloride in the organic phase below ca 0.96 M there seems to be no strong TBP–electrolyte interaction as occurs for example in the extraction of nitric acid by TBP.[(1,7,11,17)] The discontinuities in the plots of physical chemical properties which arise when 5.1 mmole of lithium chloride have been extracted ($[\mathrm{LiCl}]_0 \sim 0.96$ M) correspond to a H_2O:LiCl mole ratio in the organic layer of four. It appears therefore that lithium chloride in the organic phase has a tendency to maintain a primary hydration number of four. This is borne out by the fact that after 5.1 mmole of LiCl have been extracted there is an increased tendency for water to be extracted relative to lithium chloride until 6.1 mmole of LiCl have entered the organic phase. When more than 5.1 mmole of LiCl are extracted TBP molecules begin to substitute for water molecules in the solvation shell of the extracted alkali chloride. However, a solvation number of four appears to be maintained and in the almost saturated solution, when 10.098 mmole of LiCl have entered the organic phase, the ratio (TBP + H_2O):LiCl is equal to four. The stage at which lithium chloride begins to enter the organic layer without accompanying water molecules commences when the H_2O/LiCl mole ratio in the equilibrium *aqueous* phase is four. This suggests that in concentrated aqueous solution lithium chloride tends to maintain a hydration number of four.

There is additional evidence for the latter conclusion. Glueckauf[(18)] has obtained a value of 4.3 for the hydration number of LiCl by application of his equation for activity coefficients in concentrated electrolyte solutions to tabulated experimental data.[(19,20)] Moreover, application of the Brunauer, Emmett and Teller adsorption isotherm[(21)] to very concentrated aqueous solutions of lithium chloride indicates that the electrolyte has four sites for the "adsorption" of water molecules.[(22)] Also, from a comparison of viscosity and apparent molar volume data Stokes[(23)] concludes that in concentrated aqueous solutions of lithium chloride the number of "bound" water molecules is 3.4.

[(16)] J. Chien-Han Chi, Univ. Michigan, Microf. diss. 1943, No. 1169, abstr. IX, 2, 1949.

[(17)] E. Hesford and H. A. C. McKay, *J. Inorg. Nucl. Chem.* **13**, 156 (1960).

[(18)] E. Glueckauf, *Trans. Faraday Soc.* **51**, 1235 (1955).

[(19)] R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.* **45**, 612 (1949).

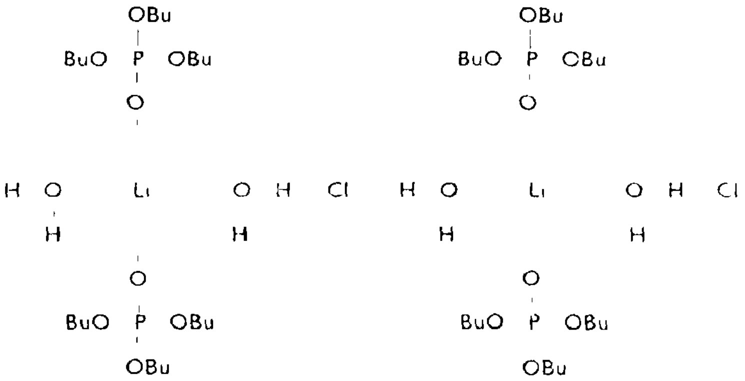
[(20)] R. H. Stokes, *Trans. Faraday Soc.* **44**, 295 (1948).

[(21)] S. Brunauer, P. H. Emmett, and E. Teller, *J. Amer. Chem. Soc.* **70**, 1870 (1948).

[(22)] R. A. Robinson and R. H. Stokes, *Electrolyte Solutions* (2nd Ed.) Chap. 3. Butterworths, London (1959).

[(23)] R. H. Stokes, in W. J. Hamer (Ed.), *The Structure of Electrolytic Solutions*, p. 298, Wiley, New York, Chapman Hall, London (1959).

The extremely high viscosities of TBP extracts from very strong aqueous solutions of lithium chloride may be due to the formation of aggregations (cf. BELLO and BELLO[24,25]) such as



In these formulae dots may be regarded as indicating hydrogen bonds and dashes ion-dipole interactions. The extracts show mixing lines on shaking which is compatible with the formation of such aggregates. Cases of lithium salts forming solvates with dipolar aprotic solvents and yielding extremely viscous solutions have been reported elsewhere.[26]

Acknowledgements. The conductivity measurements described in the present paper were performed at Chelsea College of Science and Technology. Grateful acknowledgement is made to Dr. J. F. J. DIPPY, Dr. S. R. C. HUGHES and Mr. S. WHITE for helpful advice and for putting apparatus at the disposal of the authors.

Mr. S. THORBURN is to be thanked for valuable help with the gas chromatographic measurements.

[24] J. BELLO and H. R. BELLO, *Nature Lond.* **190**, 440 (1961).
[25] J. BELLO and H. R. BELLO, *Nature Lond.* **194**, 681 (1962).
[26] A. J. PARKER, *Quart. Rev.* **16**, 163 (1962).

J. Inorg. Nucl. Chem. 1963. Vol. 25, pp. 303 to 327. Pergamon Press Ltd. Printed in Northern Ireland

NOTES

Phthalocyaninoruthenium derivatives[1]

(*Received* 11 *July* 1962)

PHTHALOCYANINOIRON(II) and manganese(II) exist both as simple compounds and as amine adducts. Also, both elements have been reported to form phthalocyanino derivatives in which the central element is in a higher oxidation state.[2-5]

Work on the phthalocyaninoruthenium system has revealed some differences between its behaviour and that of the iron and manganese systems. Isolation and identification of ruthenium species other than those of ruthenium(II) have not been accomplished. (Nor has a repetition of the air-HCl oxida*tion of PcFe*[5] *been effected; however apparently an HCl adduct of the ring nitrogens of PcFe*[6] has been observed correlating with recently reported work on PcFe.[7]) The relative stability of the Ru^{II} (d^6) must be associated with the special features of the aromatic, planar, quadridentate phthalocyanino ligand. In the amine adducts the Ru is probably octahedrally coordinated, two amines occupying the *trans* positions, while in PcRu the Ru is likely coordinated in a square planar fashion.

PcRu·$6C_6H_5NH_2$

A 1.00 g sample of $RuCl_3$ (4.8 mmole) was heated with 9.00 g of *o*-cyanobenzamide[8] (unpurified) at 270°C for 2 hr. After twice heating the resulting product with 20 ml of glacial acetic acid at reflux for 5 min, washing with water and drying, 1.67 g of powdered blue-black PcRu was obtained. Crystallization of this product from 6.0 ml of aniline yielded 1.15 g of crystals with a typical phthalocyanine appearance (red reflection, blue transmission). Recrystallization of these from 5.0 ml of aniline followed by vacuum drying gave 0.58 g (0.49 mmole) of PcRu·$6C_6H_5NH_2$. Found: C, 69.47; H, 5.21; Ru, 8.19; aniline, 47.7. Calc. for $C_{32}H_{16}N_8Ru·6C_6H_7N$: C, 69.67; H, 4.99; Ru, 8.62; aniline, 47.70. Aniline was determined by potentiometric titration with $HClO_4$ in acetic acid. The solutions of aniline used for titration were prepared by treatment of the adduct with hot acetonitrile followed by filtration of the resulting solution to remove the interfering PcRu residue.

PcRu·6*o*-$CH_3C_6H_4NH_2$

A 1.00 g sample of $RuCl_3$ (4.8 mmole) was heated with 9.00 g of *o*-cyanobenzamide (unpurified) at 270°C for 2 hr. After the resulting product was extracted with glacial acetic acid for 24 hr, washed with water and dried, 2.00 g of powdered blue-black PcRu was obtained. Crystallization of this 2.00 g (3.26 mmole) of PcRu from 6.0 ml of *o*-toluidine followed by recrystallization of the product from 3.0 ml of *o*-toluidine yielded, after vacuum drying, 0.40 g (0.32 mmole) of crystalline PcRu·6*o*-$CH_3C_6H_4NH_2$. Found: C, 70.48; H, 5.71; Ru, 8.32; *o*-toluidine, 50.7. Calc. for $C_{32}H_{16}N_8Ru·6C_7H_9N$: C, 70.73; H, 5.62; Ru, 8.05; *o*-toluidine, 51.2%. *o*-Toluidine was determined by a method analogous to that used with aniline.

The product left after extraction of the amine adducts with acetonitrile was apparently relatively pure PcRu. Analysis of a sample that had been extracted twice with acetonitrile and dried at 110°C gave the following results. Found: C, 62.32; H, 3.38; N, 17.90. Calc. for $C_{32}H_{16}N_8Ru$: C, 62.64; H, 2.63; N, 18.27%. Vacuum sublimation of PcRu at up to 600° gave low yields of poorly formed crystals. Under similar conditions, PcFe gave good sublimates. Infrared spectra of samples of PcRu that had been heated suggested that a second polymorphic modification was formed, an unsurprising observation in view of the polymorphism of other bivalent transition metal phthalocyanines.[9] Treatment of PcRu with concentrated H_2SO_4 did not produce PcH_2 in contrast to the reported behaviour of PcMn. PcRu formed adducts with other amines such as pyridine but these were not further investigated.

---

[1] This work was supported in part by National Science Foundation Grant No. G-15833.

[2] P. A. BARRETT, C. E. DENT and R. P. LINSTEAD, *J. Chem. Soc.* 1719 (1936).

[3] J. S. ANDERSON, E. F. BRADBROOK, A. H. COOK and R. P. LINSTEAD, *J. Chem. Soc.* 1151 (1938).

[4] P. A. BARRETT, D. A. FRYE and R. P. LINSTEAD, *J. Chem. Soc.* 1157 (1938).

[5] J. A. ELVIDGE and A. B. P. LEVER, *Proc. Chem. Soc.* 195 (1959).

[6] Pc = $C_{32}H_{16}N_8$.

[7] A. N. SIDOROV and A. N. TERENIN, *Opt. Spectrosc.* **11**, 175 (1961).

[8] G. T. BYRNE, R. P. LINSTEAD and A. R. LOWE, *J. Chem. Soc.* 1017 (1934).

Spectra

Bands useful for identification of these compounds in the 650–1150 cm^{-1} region in Nujol suspension are: PcRu·6C H N, 695, 730, [illegible], 7?7, 88?, 914, 1006, 1027, 1067, 1093, 1126; PcRu·6C H N, 718, 7?1, 757, [illegible], 915, 1006, 106?, 1094, 1123; PcRu, 733, [illegible], 778, 871, 912, 943, 1006, 1064, 1122. The visible spectra of the compounds in benzene show the following maxima (in mμ): PcRu·6C H N, 6?2, ?80, ?7?; PcRu·6C H N, 632, 582, [illegible]; PcRu, 645, 584.

P. C. KRUEGER
M. E. KENNEY

Department of Chemistry
Case Institute of Technology
Cleveland 6, Ohio

[9] A. N. SIDOROV and I. P. KOTLYAR, *Opt. Spectrosc.* **11**, 92 (1961).

On the synergistic effect in solvent extraction

(*Received* 18 *June* 1962)

RECENTLY a number of papers have appeared which deal with the nature of the species that cause a synergistic effect in solvent extraction systems containing thenoyltrifluoroacetone (TTA) and a phosphate ester.[1,2] Most of the attention has been directed to studies of the actinide elements but HEALY has also investigated some rare earths and alkaline earths. It has been found that the phenomenon can be explained by an organic phase reaction whereby there is an addition of one or two molecules of a phosphate ester onto the neutral TTA complex of the metal.

The question of how a phosphate ester can add onto a tetravalent actinide which is coordinately saturated by TTA is one which is difficult to answer. In fact this problem led IRVING and EDGINGTON[1b] to predict that the synergistic effect should not be observed in the extraction of the tetravalent actinides. However, in a later study on the extraction of the tetravalent actinides with TTA and TBP (tri-butylphosphate) they in fact observed a synergistic effect.[1c] They were able to analyse their results in terms of a displacement of TTA by TBP and nitrate ion. As an example, for thorium they postulate species such as $ThT_3(NO_3)(TBP)$ and $ThT_2(NO_3)_2(TBP)_2$ where T^- is the enolate ion of TTA. Although their prediction was wrong, they nevertheless were not faced with the problem of postulating a molecule in which the coordination saturation is apparently exceeded. Although not pertinent to their argument, it should be pointed out that the formulations of their equilibrium constants are improper. For example, in the equation

$$K_{o,a} = \frac{[ThT_3(NO_3)(TBP)]_o[H^+]_a^3}{[Th^{4+}]_a[HT]_o^3[HNO_3]_a[TBP]_o} \tag{1}$$

where the aqueous phase is designated by *a* and the organic phase by *o*, the nitric acid term in the aqueous phase should be written as the product of hydrogen and nitrate ions and consequently the equation properly written is

$$K'_{o,a} = \frac{[ThT_3(NO_3)(TBP)]_o[H^+]_a^3}{[Th^{4+}]_a[HT]_o^3[NO_3^-]_a[TBP]_o} \tag{2}$$

In the study of IRVING and EDGINGTON,[1c] the measurements were made under conditions of fixed acid and nitrate ion concentrations and consequently this problem was not recognised. The studies conducted with thorium were performed at 0·1 *M* HNO_3, and would have led to reporting values for stability constants which were low by a factor of ten for the species with one molecule of nitrate and low by a factor of 100 for the species with two nitrate molecules. They did not report values of the stability constants for the postulated thorium reactions. Fortunately, the studies conducted with neptunium and plutonium were performed at 1·0 *M* nitric acid and consequently, the values reported for the stability constants are correct if the formulations are rewritten to conform with equation (2).

[1] H. IRVING and D. N. EDGINGTON, (a) *J. Inorg. Nucl. Chem.* **15**, 158 (1960); (b), *Ibid.* **20**, 314 (1961); (c) *Ibid.* **20**, 321 (1961); (d), *Ibid.* **21**, 169 (1961).

[2] T. V. HEALY (a) *J. Inorg. Nucl. Chem.* **19**, 314 (1961); (b) *Ibid.* **19**, 328 (1961).

Although the results of IRVING and EDGINGTON suggest that the synergistic effect for the tetravalent actinides takes place only by a replacement of a TTA molecule, HEALY(2) found that a synergistic effect can occur as a consequence of addition without replacement. HEALY also examined the TTA/TBP system, but utilized an aqueous phase containing hydrochloric acid instead of nitric. It is apparently this difference which permits the occurrence of an addition reaction as opposed to a replacement reaction to take place for the tetravalent actinides. In a nitrate medium there is a competition between the extraction by TBP of the thorium nitrate complex and the extraction by TTA of the thorium ion. The consequence is a mixed ligand complex which contains thorium, nitrate, TBP and TTA. In a chloride medium where there is no competition due to the extraction of a thorium chloride complex by TBP, the synergism occurs by means of an addition reaction. Therefore it is apparent that the replacement mechanism arises solely from the phenomenon of competitive equilibria and is not inherent to the problem of the actinide being coordinately saturated.

In a recently completed study NEWMAN and KLOTZ(3) have shown that there is a synergistic effect by tri-*n*-octylamine (R_3N) on the solvent extraction of thorium by TTA. The species which was postulated to account for the synergistic effect is ThT_4R_3NHCl and consequently an addition reaction is also observed for a tetravalent actinide element in a somewhat different solvent extraction system than employed by any of the previous workers. The argument was put forth that the R_3NHCl was bound by means of one of the TTA molecules and not the thorium. The data of HEALY permits an extension of this argument to the solvent extraction systems and metals that were studied in his investigation.

HEALY obtained extensive data for evaluating the overall equilibrium constants for various metals by solvent extraction systems containing TTA with TBP or TOPO (tri-*n*-octylphosphine oxide). The overall equilibrium constant, K_s is defined as

$$K_s = \frac{(\overline{MT_nS_s})(H^+)^n}{(M^{+n})(\overline{HT})^n(\overline{S})^s} \tag{3}$$

where M represents the metal involved in the extraction and S either TBP or TOPO. A compilation of the species which were observed and the logarithm of the overall equilibrium constants is presented in Table 1. Two diluents were investigated and the data obtained for both benzene and cyclohexane

TABLE 1.—COMPILATION OF EQUILIBRIUM CONSTANTS DESCRIBING THE SYNERGISTIC EFFECT

Species	log K_T[a]	Benzene				Cyclohexane			
		TBP		TOPO		TBP		TOPO	
		log K_s	log K_a	log K_s	log K_a	log K_s	log K_a	log K_s	log K_a
ThT_4S	1.00	5.70	4.7	7.70	6.7	7.85	6.9	10.45	9.5
UO_2T_2S	2.26	2.48	4.7		–	3.56	5.8		
$UO_2T_2S_2$	2.26			8.61	10.9			4.56	11.8
AmT_3S_2	7.46	0.96	6.5	2.51	10.0	2.34	9.8	5.20	12.7
CmT_3S_2	7.10	0.70	6.4	2.83	9.9	2.60	9.7	5.53	12.6
PmT_3S_2	7.77[b]	1.04	6.7	2.43	10.2	2.26	10.0	5.13	12.9
TmT_3S_2	6.96	0.34	6.6			2.96	9.9		
CaT_2S_2	12.00	5.27[c]	6.7	3.27	8.7	3.27	8.8	1.99	10.1

a Taken from the compilation of POSKANZER and FOREMAN, reference 4.
b Taken from HEALY, reference 2b.
c Estimated on the basis that doubly charged cations have a distribution ratio one fourth as large in benzene than in cyclohexane (Table II in HEALY, reference 2b).

have been included. Also included in the Table are the logarithms for the overall equilibrium constants K_T for the TTA extraction of each of the metals. This constant is defined as

$$K_T = \frac{(\overline{MT_n})(H^+)^n}{(M^{+n})(\overline{HT})^n} \tag{4}$$

These values were taken out of the compilation of POSKANZER and FOREMAN(4) and were measured with benzene as the diluent.

---

[3] L. NEWMAN and P. KLOTZ, *J. Phys. Chem.* In press.

[4] A. M. POSKANZER and B. M. FOREMAN, *J. Inorg. Nucl. Chem.* **16**, 323 (1961).

The actual synergistic effect can best be evaluated by the organic phase reaction

$$MT_2 + pS = MT_2S_p \tag{5}$$

Then the equilibrium constant for this reaction is

$$K_S = \frac{(MT_2S_p)}{(MT_2)(S)^p} \tag{6}$$

which can be obtained by dividing K_D by K_T. Although there may be a thousand fold increase in K_D on going from a benzene diluent to cyclohexane as the diluent, there is generally less than a ten fold change in the value of K_T. Consequently, it was possible to use the values of K_T measured for benzene in conjunction with K_D measured for cyclohexane in order to calculate a value of K_S for cyclohexane. A summary of the logarithm of the values calculated for both diluents is included in the Table.

It is significant to note that the values for the synergistic constant in a given solvent and for a given synergistic producing agent fall into two groups. In one group there is a single synergistic producing molecule per compound and in the second group two synergistic producing molecules. Considering the differences in the metals involved, it is remarkable to note the constancy of the values for K_S within each group. This is especially significant since the values of K_T used in the calculation differed by as much as twelve orders of magnitude. Since the synergistic constant is a function only of the number of atoms per molecule and not a function of the metal involved, then the synergistic producing agent most likely forms a bond with one of the TTA molecules which is attached to the metal and not directly to the metal itself. If the bond existed between the synergistic agent and the metal there should be differences in the values of K_S which reflect the differences in the metals just as these differences are reflected by the variations in the observed values for K_T. Finally, it can be concluded that the differences between the constants for the species containing one synergistic producing agent and the species containing two is an indication of the stability of the addition of the second molecule.

L. NEWMAN

Brookhaven National Laboratory
Associated Universities
Upton, Long Island, New York

Mechanism of an oxidation of Cr(II) in the presence of pyrophosphate

KRUSE and TAUBE[1] have shown that Cl^- accelerates the rate of Cr(II) reduction of both $Co(NH_3)_5H_2O^{+3}$ and also $Co(NH_3)_6^{+3}$. The latter catalysis must involve an anion effect on a reduction which proceeds by the "outer sphere" mechanism.[2]

The reduction of $Co(NH_3)_5Cl^{+2}$ by Cr^{+2} is accelerated by pyrophosphates. TAUBE[3] has presented evidence that the principal Cr(III) product of this reaction contains both chloride and pyrophosphate, indicating that this reaction involves a "non-bridging"[4] effect of pyrophosphate on a mechanism involving a chloride bridge. It seems possible that at least a portion of the effect of pyrophosphate may be similar to the Cl^- effect on the reduction of $Co(NH_3)_6^{+3}$ and may involve an outer sphere path.

We have reinvestigated the pyrophosphate system[5] to estimate the importance of the outer sphere path. $Co(NH_3)_5Cl^{+2}$ and $Co(NH_3)_5H_2O^{+3}$ were reduced with less than equivalent quantities of Cr(II) in aqueous solutions of pH 1.0 under purified N_2. In many experiments pyrophosphate was present in the same concentration (0.017–0.040 M) as the oxidant. Immediately after reduction, Ag^+ was added to determine Cl^- liberated during the reduction. Sodium salts of anions and perchlorate salts of cations were used.

No precipitate was observed when Ag^+ was added to systems in which $Co(NH_3)_5H_2O^{+3}$ had been reduced by Cr(II), whether or not $H_2P_2O_7^{-2}$ was present. No AgCl was observed when $Co(NH_3)_5Cl^{+2}$ was reduced in the absence of $H_2P_2O_7^{-2}$. When pyrophosphate was present during the reduction of $Co(NH_3)_5Cl^{+2}$ turbidity developed immediately on addition of Ag^+. Turbidity was less when reactions were carried out at 2° than when they were carried out at 25°C. As Ag^+ containing mixtures were allowed to stand, slow formation of AgCl was noted at both temperatures. In order to estimate the initial amount of free Cl^- in solution, several mixtures were spun in an ultracentrifuge immediately after Ag^+ ion was added. The amount of AgCl recovered by efficient filtration after centrifuging for several minutes was always less than 10 per cent of the amount of $Co(NH_3)_5Cl^{+2}$ reduced.

---

[1] W. KRUSE and H. TAUBE, *J. Amer. Chem. Soc.* **82,** 526 (1960).
[2] J. HALPERN, *Quart. Revs.* **15,** 207 (1961).
[3] H. TAUBE, *J. Amer. Chem. Soc.* **77,** 4481 (1955).
[4] J. HUNT and J. EARLEY, *J. Amer. Chem. Soc.* **82,** 5312 (1960).
[5] J. GØRBITZ, M.Sc. Thesis, Georgetown Univ. 1962.

The products of the reaction were separated by ion exchange columns. The initial Cr(III) product had absorption peaks at 438 and 622 mμ. During a period of several hours these peaks shifted gradually, becoming fixed at 431 and 610 mμ, the positions observed for $CrP_2O_7H_2$. Analysis showed that the original Cr(III) product had a P/Cr ratio of 2.0.

These results support the previous conclusion(4) that the major path of the reduction leads to a product in which both Cl^- and pyrophosphate are bonded to Cr(III). The slow change in the spectrum of this product and the slow formation of AgCl indicate that this species releases Cl^- at an appreciable rate.

The small amount of Cl^- free in solution immediately after reaction may indicate attack of Cr(II) on the pyrophosphate of the initial product or, less probably, contribution due to the outer sphere path. It seems certain that pyrophosphate increases the rate of the reduction primarily by a non-bridging ligand effect on the inner sphere reaction path.

We are grateful for support by the National Science Foundation.

J. E. EARLEY
J. H. GORBITZ

Department of Chemistry
Georgetown University
Washington, D.C.

Preparation of disilanyl chloride and disilanyl bromide by the reaction of disilane with hydrogen halide*

IN PREVIOUS communications we have described the preparation of disilanyl chloride(1) H_3SiSiH_2Cl and bromide(2) H_3SiSiH_2Br by the reaction of H_3SiSiH_2I with AgCl and AgBr respectively. STOCK and SOMIESKI had attempted unsuccessfully to prepare the above compounds by the direct reaction of Si_2H_6 with HCl and HBr respectively in the presence of the appropriate aluminum halide catalyst.(3) They found, that although the desired reaction occurred, the H_3SiSiH_2Cl and H_3SiSiH_2Br could not be obtained in the pure state, since they underwent disproportionation even at low temperatures. We have since shown(1,2) that this disproportionation is catalysed by small amounts of hydrogen halide and/or aluminum halide.

In the present investigation it was found that pure, stable H_3SiSiH_2Cl and H_3SiSiH_2Br could be obtained from the reaction of Si_2H_6 with HCl or HBr if the products were carefully purified. Although considerable quantities of higher halides are formed in these reactions, this appears to be the best method of preparation of disilanyl bromide which is a most useful starting material for the synthesis of other disilanyl compounds since it may be readily distilled in the vacuum system.

It is of interest to note that although HCl and HI(4) react relatively slowly with Si_2H_6 at room temperature, the analogous reaction with HBr appears to be almost instantaneous (5–6 min) both at room temperature and at −78°C.

EXPERIMENTAL

All work was carried out in a Pyrex glass vacuum system. All apparatus, instruments and techniques used were similar to those previously described.(1,4) Disilane was prepared by the reduction of Si_2Cl_6 with $LiAlH_4$.(6) Commercial anhydrous HCl, HBr, Al_2Cl_6 and Al_2Br_6 were used without further purification.

---

* This research is in part a contribution from the Laboratory for Research on the Structure of Matter, University of Pennsylvania, supported by the Advanced Research Projects Agency, Office of the Secretary of Defense. Reproduction in whole or in part is permitted for any purpose of the United States Government. This report is based on portions of theses to be submitted by M. Abedini and H. Van Dyke to the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degrees of Doctor of Philosophy.

A. D. CRAIG, J. V. URENOVITCH and A. G. MACDIARMID, *J. Chem. Soc.* 548 (1962).
L. G. L. WARD and A. G. MACDIARMID, *J. Inorg. Nucl. Chem.* **20**, 345 (1961).
A. STOCK and K. SOMIESKI, *Ber.* **53**, 759 (1920).
L. G. L. WARD and A. G. MACDIARMID, *J. Amer. Chem. Soc.* **82**, 2151 (1960).
L. G. L. WARD and A. G. MACDIARMID, *J. Inorg. Nucl. Chem.* **21**, 287 (1961).
G. W. BETHKE and M. K. WILSON, *J. Chem. Phys.* **26**, 1107 (1957).

Preparation of H_3SiSiH_2Cl

Approximately 0.5 g of anhydrous Al_2Cl_6 was placed in a side-arm tube which was attached to a 2 l bulb connected to the vacuum system. The side arm was then heated gently in order to sublime the Al_2Cl_6 [illegible]. Disilane (56 mmoles) and HCl (18 mmoles) were condensed on top of the Al_2Cl_6 in the side-arm tube which was then held at −78°C for 1 hr. The fact that no hydrogen was evolved during this time showed that no reaction of the type

$$Si_2H_6 + HCl \rightarrow H_3SiSiH_2Cl + H_2$$

had taken place. The side arm and 2 l bulb were then allowed to stand at room temperature for 8 hr. Hydrogen was evolved constantly throughout this period. Since Al_2Cl_6 is known to catalyse the decomposition of H_3SiSiH_2Cl, the reaction was stopped at this stage, the hydrogen was pumped away through several traps immersed in liquid nitrogen, and the remaining volatile material was fractionated by means of a low-temperature fractionating column somewhat similar to that described by COATES[7].

As column temperature was raised from approximately −134° to −108°, unreacted HCl and Si_2H_6 distilled over. At temperatures from −108° to −75° crude H_3SiSiH_2Cl was obtained while higher chlorodisilanes remained as a residue. Careful redistillation of the crude H_3SiSiH_2Cl finally yielded the pure material (0.20 mmole, mol. wt. found 97.3, calc. 96.7, vapour pressure at −45.3°C found 11.1 mm, literature 11.2 mm[1], infrared spectrum identical to that of the pure material[1]). The infrared spectra of other fractions obtained in this distillation indicated that these also contained H_3SiSiH_2Cl contaminated with varying quantities of presumably $Si_2H_4Cl_2$. The presence of even small amounts of higher chlorides in the H_3SiSiH_2Cl could be recognized readily by a characteristic strong infrared absorption doublet at 769 cm^{-1} and 776 cm^{-1} of almost equal intensities. Whereas the infrared spectrum of H_3SiSiH_2Cl had previously been measured only in the 4000 cm^{-1} to 667 cm^{-1} region by means of a Perkin-Elmer model 137B Infracord spectrophotometer, the sample obtained in this research was examined in the 4000 cm^{-1} to 550 cm^{-1} region by means of a Perkin-Elmer model 421 grating spectrophotometer. The Si–H stretching absorption previously reported at 2190 cm^{-1} was found to be resolved into a well-defined doublet at 2164 cm^{-1} and 2180 cm^{-1} of almost equal intensities. The values obtained with the 421 spectrophotometer are considered to be more accurate than those given by the Infracord instrument.

Additional evidence for the purity of the H_3SiSiH_2Cl obtained as described above is given by the fact that negligible decomposition occurred at −45° during an eight-hour period. A sample having a vapour pressure of 11.3 mm at −45.2° (literature value[1], 11.3 mm) was placed in an all-glass tensimeter fitted with mercury seals. The vapour pressure at −45.2° rose during 20 min to 12.5 mm and then remained constant at this value for the next 7.5 hr. 0.15 mm pressure of non-condensable gas was present at the end of the experiment and the infrared spectrum of the whole sample was identical to that of the starting material. The small rise in pressure at the beginning of the experiment is not surprising, for unless the surfaces of a tensimeter have been thoroughly pre-treated with the pure compound, a slight change in pressure is frequently observed. This is presumably due to reaction of the compound with traces of material absorbed on the glass.

Although excess Si_2H_6 was used in the initial reaction, some HCl mixed with a little SiH_4, was recovered unchanged as a fraction which distilled through a −134°C trap (mol. wt. found, 37.4, calc., 36.5; strong positive test for Cl⁻ after hydrolysis; infrared spectrum showed the presence of some SiH_4). Disilane (47.6 mmole, mol. wt. found 56.6, calc. 62.2, infrared spectrum identical to that of pure material[8]) which appeared to be contaminated with HCl was also isolated.

Preparation of H_3SiSiH_2Br

Si_2H_6 (42 mmole) and HBr (14 mmole) were condensed into an approximately 120 ml tube containing Al_2Br_6 (~1 g) which had previously been sublimed *in vacuo* as a layer on the lower walls of the tube. That part of the tube containing the reactants and catalyst was then surrounded by a −78° bath for 6 min. Much hydrogen was evolved during this period but only a slight amount was evolved during the next 6 min.

Hydrogen was removed from the other volatile materials by pumping the contents of the tube through five traps immersed in liquid nitrogen. Excess Si_2H_6 (33 mmoles, mol. wt. found, 62.0, calc. 62.1) was separated from the reaction products by distillation through a −96°C trap connected to a trap immersed in liquid nitrogen. The bromodisilanes which collected in the −96°C trap were then transferred to the low temperature fractionating column and upon distillation, a small amount of Si_2H_6 (column temperature −96°C) and then pure H_3SiSiH_2Br (column temperature −64°C, 1.09 mmole, mol. wt. found, 141.1, calc., 141.1, vapour pressure at 0°C found, 44.1 mm, literature

---

(7) G. F. COATES, *J. Chem. Soc.* 2003 (1951).

(8) H. S. GUTOWSKY and E. O. STEJSKAL, *J. Chem. Phys.* **22**, 939 (1954).

value[2] 45·0 mm.) were obtained. All the HBr had been consumed in the reaction and in addition to the H_3SiSiH_2Br, large quantities of higher bromodisilanes were also produced.

Disilanyl bromide was conveniently prepared on a large scale for use in subsequent syntheses as shown by the typical experiment given below. Si_2H_6 (126 mmole) and HBr (42 mmole) were condensed in a side-arm tube connected to a 5 l. reaction bulb which contained Al_2Br_6 (~0·5 g) sublimed on its inner walls. The Si_2H_6 and HBr were allowed to vapourize into the reaction bulb and after 5 min at room temperature Si_2H_6 (109 mmole; mol. wt. found, 62·0, calc. 62·1; infrared spectrum identical to that of pure Si_2H_6,(8, 9)) and pure H_3SiSiH_2Br (7·68 mmole; 18 per cent yield; mol. wt. found 141·4, calc. 141·1; vapour pressure at 0°, found, 45·5 mm; literature value[2] 45·0 mm) were recovered from the reaction products as described above. A further 5·1 mmole of slightly impure material (mol. wt. found 145·0; vapour pressure at 0°, found, 39·8 mm) which could be used as such for most syntheses was also obtained. No unreacted HBr was recovered from the reaction products. Large quantities of less volatile higher bromodisilanes remained in the fractionating column. The purity of the H_3SiSiH_2Br was further confirmed by the fact that it underwent only slight decomposition on standing at 0°C for 24 hr in a glass tensimeter fitted with mercury seals. The vapour pressure at the beginning of the experiment was 45·5 mm and after 24 hr it had increased to only 49·9 mm; 1·15 mm of non-condensable gas was present at the end of the experiment.

The infrared spectrum of H_3SiSiH_2Br was measured in the 4000 cm^{-1}–550 cm^{-1} region by means of a Perkin Elmer Model 421 spectrophotometer. The Si–H stretching absorption previously reported at 2190 cm^{-1} using a Perkin-Elmer Model 137B Infracord spectrophotometer was found to be resolved into a well-defined doublet at 2162 cm^{-1} and 2178 cm^{-1} of equal intensities.

John Harrison Laboratory of Chemistry
University of Pennsylvania
Philadelphia 4, Pennsylvania

M. Abedini
C. H. Van Dyke*
A. G. MacDiarmid†

* Union Carbide Fellow.
† Alfred P. Sloan Research Fellow.

Annealing of chemical radiation damage in crystalline barium nitrate

(*Received* 10 *September* 1962)

Maddock and Mohanty[1-3] have shown that when certain irradiated crystalline nitrates are heated the damage fragments, namely nitrite ions and oxygen, which remains trapped in the lattice recombine to form the original nitrate. The authors[1] observed a very small annealing in electron bombarded barium nitrate. No kinetic studies were made. The present communication reports results on isothermal annealing kinetics of γ-irradiated barium nitrate.

Analytical grade barium nitrate was used as received, the crystals varying in the 30–100 mesh range. The crystals were dried over phosphorus pentoxide. Samples sealed *in vacuo* in Pyrex ampoules were irradiated with ^{60}Co γ-rays to doses of about 50 Mrad. The dose rate was 1·68 × 10^{6} rad/hr. The irradiated crystals were preserved in desiccators over phosphorus pentoxide before examination or thermal treatment. Isothermal annealing runs were made in ampoules in a thermostatic electric hot air oven maintained to within ±1°C of the desired temperature. The damage nitrite was estimated spectrophotometrically with a Beckman model DU quartz instrument.

Irradiation produced a faint yellow-brown colouration of the crystals. The colouration disappeared completely within about 1 hr of thermal annealing.

Results on isothermal annealing of the chemical damage at different temperatures are shown in the Fig. 1. The fraction annealed is given by

$$\{[NO_2^-]_0 - [NO_2^-]_t\}/[NO_2^-]_0$$

where $[NO_2^-]_0$ is the initial nitrite content of the irradiated crystals and $[NO_2^-]_t$ the nitrite content at time t. The initial nitrite content was 3311–3324 p.p.m. It is seen that the annealing pattern is similar to that obtained in other systems, that is, an initial rapid reaction followed by a monotonically slow one. The recovery is rather small; the fraction recovered over 50 hr at 275°C is only 0·168.

[1] A. G. Maddock and S. R. Mohanty, *Nature, Lond.* **182**, 1797 (1958).
[2] A. G. Maddock and S. R. Mohanty, *Disc. Faraday Soc.* 31, 193 (1961).
[3] A. G. Maddock and S. R. Mohanty, *Radiochim. Acta* (in Press).

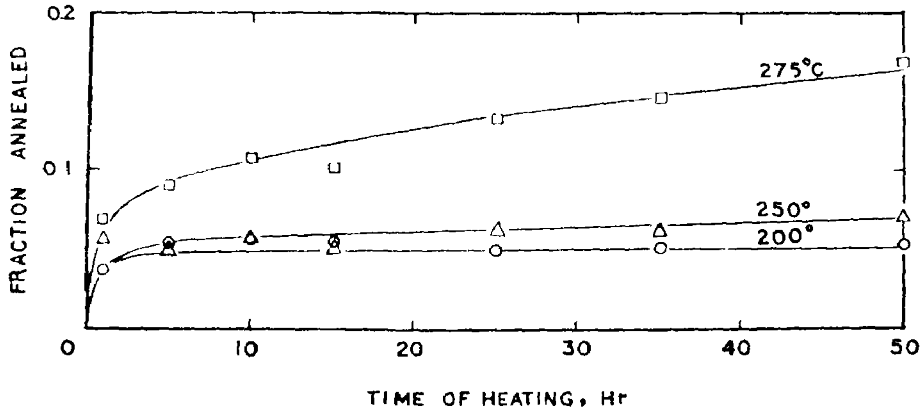


FIG. 1

Barium nitrate is stable up to red heat temperatures.[1] Two estimates in the literature[2,3] of the temperature for the onset of thermal decomposition of barium nitrite give 362 and 270°C. In the present set of experiments the nitrite content (0.1 %) of synthetic mixed crystals of barium nitrate–barium nitrite was virtually unchanged when heated for 50 hr at 275°C. Thus the disappearance of the damage nitrite on annealing does not arise from a normal thermal decomposition of barium nitrite dispersed in the nitrate matrix. The possibility that the effect is due to atmospheric oxidation has already been excluded by MADDOCK and MOHANTY.[3,4] The diminution of the damage nitrite in barium nitrate as in other nitrates is therefore a true annealing phenomenon.

Acknowledgements—We are indebted to the Atomic Energy Establishment Trombay for the irradiations which were performed with the Gamma-Ray and Sterilization Unit presented by the Government of the U.S.A. One of us (S. R. U.) gratefully acknowledges the award of a scholarship by the Ministry of Scientific Research and Cultural Affairs, Government of India.

Radiochemical Laboratory
Department of Chemistry
Banaras Hindu University
India

S. R. MOHANTY
S. R. UPADHYAY

---

[1] J. F. THORPE and M. A. WHITELEY, *Thorpe's Dictionary of Applied Chemistry* Vol. **1**, p. 639. Longmans Green, London (1937).
M. TZENTNERSHVER and W. PIEKIELNY, *Bull. intern. acad. polonaise Classe sci. math. nat.* 389 (1933).
[3] J. BUREAU, *Ann. chim.* **8**, 5 (1937).

Crystal structure of thorium perchlorate tetrahydrate by X-ray method

(*Received* 23 *October* 1962)

CRYSTALS of thorium perchlorate were prepared by dissolving freshly precipitated and purified thorium hydroxide in perchloric acid in 1:4 mole ratio. The resultant clear solution was evaporated by passing dry air at room temperature, when crystals were formed. The crystals were separated from the mother liquor and recrystallized from 0.2 N perchloric acid solution. The crystals were then dried to constant weight over phosphorus pentoxide under vacuum in a desiccator. The crystals were colourless plates and extremely hygroscopic. When examined under polarizing microscope the crystals exhibited biaxial character. Analysis of the crystals corresponded to the formula $Th(ClO_4)_4 \cdot 4H_2O$. KOLTHOFF and IKEDA[1] reported $Th(ClO_4)_4 \cdot 1.7H_2O$ starting from thorium nitrate and 70% perchloric acid. These authors dried the crystals to constant weight under vacuum at 70°C in a

[1] I. M. KOLTHOFF, S. IKEDA, *J. Phys. Chem.* **65**, 1020 (1961).

vacuum oven The difference in the water molecules of the two hydrates may be due to the temperature effect

The tetrahydrate crystals were powdered to about 300 mesh size in a dry box, filled in a 0 5 mm (I D) Lindemann glass capillary and sealed it hermetically The X-ray diffraction pattern of the substance was taken with 143 2 mm G E camera, using nickel filtered CuK_α radiation at 34 kV and

TABLE 1 — X-RAY DATA OF $Th(ClO_4)_4\ 4H_2O$

Line No	*hkl*	d-spacings observed (Å)	d-spacings calculated (Å)	Relative intensities
1	020	8 246	8 246	15
2	021	6 681	6 681	15
3	012	5 313	5 370	10
4	031	4 890	4 940	20
5	022	4 686	4 686	20
6	110	4 324	4 300	20
7	101	4 140	4 139	100
8	003	3 763	3 780	55
9	102	3 515	3 501	20
10	042	3 358	3 343	20
11	131	3 323	3 316	20
12	122	3 220	3 226	20
13	140	3 031	3 026	75
14	052	2 861	2 860	20
15	123	2 706	2 714	20
16	133	2 551	2 556	20
17	062	2 479	2 480	30
18	152	2 410	2 404	20
19	143	2 359	2 364	20
20	124	2 301	2 300	20
21	015	2 259	2 253	20
22	200	2 225	2 221	30
23	211	2 171	2 170	30
24	230	2 065	2 064	25
25	125	1 965	1 966	20
26	213	1 906	1 904	35
27	006	1 889	1 893	15
28	242	1 853	1 849	35
29	164	1 806	1 808	35
30	182	1 778	1 778	20
31	204	1 751	1 752	20
32	234	1 672	1 668	20
33	075	1 637	1 637	20
34	215	1 583	1 581	20
35	047	1 509	1 511	20
36	127	1 496	1 500	20
37	312	1 427	1 427	20
38	290	1 416	1 416	20
39	322	1 409	1 410	20
40	148	1 286	1 284	20
41	353	1 274	1 275	20
42	159	1 137	1 140	20
43	460	1 030	1 030	20
44	298	1 003	1 004	20
45	426	0 9510	0 9518	20
46	564	0 8097	0 8089	20
47	565	0 7931	0 7929	20
48	593	0 7836	0 7828	60
49	575	0 7809	0 7810	30

4 44 Å *b* 16 51 Å and *c* 11 35 Å

18 mA The specimen was rotated through 360 and exposed for 18 hr The d-spacings of the diffraction pattern were corrected for the film shrinkage The lines were indexed for orthorhombic system using Hesse and Lipson's procedure[2, 3] The observed and the calculated d-spacings according to the orthorhombic system together with the relative intensities are given in the table Relative intensities were visually assigned

The results given in the table show that there is a good agreement between the observed and the computed values for various reflections, especially for medium and high values of θ

The density of the crystals was determined by the specific gravity bottle using dry benzene as displacing liquid and was found to be 2 780 g/ml at 25 C Employing this density the number of molecules of the perchlorate per unit cell was found to be 1 982 ~ 2 From the systematic absence of the lines when h and k are odd in $h00$ and $0k0$ respectively the symmetry of the crystals may correspond to $P_{2_12_12}$ (space group No 18) The density calculated from X-ray data is 2 802 g/ml which is in good agreement with the experimental value Since the crystals are extremely hygroscopic, single crystal X-ray diffraction could not be done

Acknowledgement The authors are thankful to Dr J Shankar for helping in taking the X-ray pattern

P Rama Murthy
C C Patel

Department of Inorganic and Physical Chemistry
Indian Institute of Science
Bangalore 12 India

[2] R Hesse, *Acta Cryst* **1**, 200 (1948)
[3] H Lipson, *Acta Cryst* **2**, 43 (1949)

The partial molal volumes of OCN, SeCN, ReO_4, BF_4, SO_3F, SO_3NH_2

(*Received 4 September* 1962)

In the course of an investigation of the relationship between size of certain inorganic anions and their biological activity[1] neither the partial molal ionic volumes nor adequate density data were found to be available in the literature Density determinations of aqueous solutions of KOCN, KSeCN, $NaReO_4$, NH_4BF_4, NH_4SO_3F and $NH_4SO_3NH_2$ were carried out The partial molal volume of each salt was obtained graphically from density data by the method of Masson[2]

$$\phi_v \quad \phi_0 \quad S_v\sqrt{c}$$

where ϕ_v is apparent molal volume
ϕ_0 is the partial molal volume at infinite dilution
S_v is the slope
c is the concentration in moles l

The partial molal volumes of the anions were then obtained by subtracting the cation volumes according to the convention of Fajans and Johnson[3]

MATERIALS AND METHODS

Of the salts employed in this work $NaReO_4$ KOCN and $NH_4SO_3NH_2$ were supplied in reagent or pure form NH_4BF_4 was prepared from NH_4HF_2 and H_3BO_3 according to Booth and Rehmar[4] KSeCN (Bios Laboratories) was purified by extraction in acetone at room temperature and cold recrystallization from that solvent, this method was a modification of that by Waitkins and Shutt[5], the cold recrystallization being substituted for the distillation since some decomposition of the selenocyanate accompanied its treatment with either heat or vacuum NH_4SO_3F (Chemicals Procurement Laboratories) was purified by extraction in methanol, followed by extraction in ethanol and two-fold recrystallization from the same solvent according to Traube[6], the final product exhibited a definite melting point of 245 C, it yielded upon elemental analysis, N 11 88, S 27 03 F 16 36%, theoretical N 11 96, S 27 38, F 16 22% Double distilled water was used throughout

[1] J Wolff and J R Maurey, *Biochim Biophys Acta* **69**, 58 (1963)
[2] D O Masson, *Phil Mag* **8**, 218 (1929)
[3] K Fajans and O Johnson, *J Amer Chem Soc* **64**, 668 (1942)
[4] H S Booth and S Rehmar, *Inorganic Syntheses*, **II**, 23 (1946)
[5] G R Waitkins and R Shutt, *Inorganic Syntheses* **II**, 186 (1946)
[6] W Traube *Ber* **46**, 2525 (1913)

Absolute densities were determined at 25.0 ± 0.01°C by the pycnometric procedure described by BAUER and LEWIN(7). The volumes of the solutes were calculated from the solution densities according to the procedure described by MASSON([illegible]). The apparent volume occupied by the solute in each solution was obtained from the equation

$$\phi_V = (M_2/W_2)[(W/d) - (W_1/d_1)]$$

where ϕ_V is the apparent molal volume (ml per mole) of the solute at the specified concentration, M_2 is the molecular weight of the solute, W_2 is the mass of the solute in the solution, W is the mass of the solution, d is the density of the solution, W_1 is the mass of the water in the solution, and d_1 is the density of pure water at the temperature specified. For each salt, the apparent molal volumes were plotted versus the square roots of the molar concentrations, and the partial molal volume of the salt

TABLE 1. CONCENTRATIONS AND DENSITIES OF SOLUTIONS, AND APPARENT MOLAL VOLUMES OF SOLUTE AT 25.0°C

Salt	Concentration (%)	Concentration (molar)	Density (gm/ml)	ϕ_V (ml/mole)	Salt	Concentration (%)	Concentration (molar)	Density (gm/ml)	ϕ_V (ml/mole)
$NaReO_4$	16.24	0.6836	1.15068	48.71	NH_4BF_4	16.52	1.683	1.06812	62.82
	15.87	0.6660	1.14687	48.49		12.112	1.211	1.04812	62.85
	13.30	0.5451	1.11976	48.32		5.051	0.4903	1.01786	62.59
	10.157	0.4044	1.08807	48.34		2.591	0.2490	1.00769	62.30
	6.820	0.2636	1.05649	47.95					
	6.414	0.2471	1.05274	48.01					
	4.266	0.1613	1.03343	47.87	NH_4SO_3F	30.08	2.947	1.14737	66.30
	2.726	0.1017	1.02003	47.53		21.24	1.992	1.09881	66.23
	1.811	0.06708	1.01221	47.43		13.49	1.220	1.05947	66.14
						10.059	0.8958	1.04297	66.04
KOCN	27.88	4.023	1.17026	38.17		7.325	0.6443	1.03007	66.04
	19.03	2.606	1.11107	37.48		3.005	0.2603	1.01041	65.76
	12.714	1.679	1.07132	36.99		2.915	0.2514	1.01002	65.69
	7.628	0.9788	1.04077	36.55					
	3.906	0.4907	1.01917	36.14	$NH_4SO_3NH_2$	40.04	4.228	1.20512	65.10
	1.617	0.2005	1.00614	35.87		30.20	3.039	1.14859	64.45
						24.41	2.392	1.11827	63.63
KSeCN	42.74	3.928	1.32412	60.99		18.98	1.813	1.08990	63.10
	33.16	2.840	1.23393	60.84		13.32	1.238	1.06117	62.52
	30.73	2.587	1.21276	60.85		9.051	0.8249	1.04015	62.05
	22.34	1.778	1.14627	60.30		5.532	0.4960	1.02322	61.54
	13.30	0.9978	1.08108	60.04		2.823	0.2499	1.01045	60.65
	6.848	0.4938	1.03889	59.51					
	2.832	0.1993	1.01391	59.60					

All values for percent composition and density are corrected for buoyancy.
The percent concentration = (gm salt/gm solution) × 100%.

TABLE 2. PARTIAL MOLAL VOLUMES OF SALTS AND ANIONS AT INFINITE DILUTION AND S_V OF SALTS IN AQUEOUS SOLUTION AT 25.0°C

Salt	ϕ_0 Salt (ml/mole)	ϕ_0 Anion (ml/mole)	S_V Salt (ml mole^{-1}) (moles/l)$^{-1/2}$
$NaReO_4$	46.97	48.7	1.99
KOCN	35.14	26.7	1.48
KSeCN	58.70	50.3	1.21
NH_4BF_4	62.04	44.0	0.67
NH_4SO_3F	65.79	47.8	0.297
$NH_4SO_3NH_2$	59.35	41.4	2.84

N. BAUER and S. Z. LEWIN in WEISSBERGER, *Physical Methods of Organic Chemistry* 3, Vol. I, Part I, p. 148, Interscience Publishers, New York (1959).

at infinite dilution was obtained by extrapolating a straight line drawn through the points to zero concentration. The factor S_v was determined as the slope of the straight line.

Density determinations were also made on solutions of KI, KSCN *and* NH$_4$SCN *in order to obtain* ϕ_0 values for the anions I$^-$ and SCN$^-$ to compare with values given by *Evans and Johnson*[4]. The ϕ_0 values reported by those authors for I$^-$ and SCN$^-$ are 36.7 *ml mole*$^{-1}$ and 40.6 *ml mole*$^{-1}$ respectively; the ϕ_0 values found by our determinations were 36.8 *ml mole*$^{-1}$ for I$^-$, and 41.0 ml mole^{-1} for SCN$^-$ as either the potassium salt or as the ammonium salt.

RESULTS

The concentrations given both as percent and as molar, with the densities of the solutions and the apparent molal volumes of the solute are given for each salt in Table 1.

The partial molal volume of each salt at infinite dilution, the calculated partial molal volume of its anion at infinite dilution, and the slope S_v relating its apparent molal volume to finite molar concentrations are all given in Table 2.

J. R. Maurey
J. Wolff

National Institute of Arthritis and Metabolic Diseases
National Institutes of Health
Bethesda 14, Maryland

Distillation of ruthenium tetraoxide with volatile acids

(*Received* 29 *September* 1962)

As the boiling point of ruthenium tetraoxide is low (100°C), ruthenium can be easily separated from other elements by distillation. When the distillation is carried out with pure water, however, the yield fluctuates from 66 to 94 per cent.[1] This low yield is caused by the decomposition of ruthenium tetraoxide and the deposition of ruthenium dioxide in the hot zone of the distillation apparatus.[2]

Lately, the effect of several oxidizing agents for ruthenium was studied and the yield was improved.[3,4] The author believes that the effect of acids on the yield must be also studied.

In many cases, sulphuric acid (98.3% soln. b.p. 330°C), which is a typical non-volatile acid, has been used together with the oxidizing agents. The somewhat volatile perchloric acid (72% soln. b.p. 203°C) has also been used. In this note the distillation of ruthenium tetraoxide from solutions of volatile acids, e.g. nitric acid (69.8% soln. b.p. 123°C), acetic acid (b.p. 118°C), trifluoroacetic acid (79.4% soln. b.p. 105.5°C) or silicofluoric acid has been studied. Mixtures of these volatile acids with phosphoric or sulphuric acid were also used. The yield of ruthenium tetraoxide by distillation was measured with ruthenium-106 as the tracer.

EXPERIMENTAL

The solution of ^{106}Ru-^{106}Rh tracer (about 500 000 counts/min), potassium permanganate and water was mixed in an all-glass Claisen's distillation flask with the volatile acids and, if necessary, non-volatile acid and the mixture was distilled. The air, which escaped through the condenser, was washed in a bubbler. The initial volume decreased by about half after distilling for 30–60 min. Then the yield of ruthenium tetraoxide was determined by measuring the activity of a constant volume of the distillate, the washing solution, and the mother liquor with a well-type scintillation counter.

For experiments on a macro scale, a mixture of metallic ruthenium and ^{106}Ru-^{106}Rh tracer fused with potassium hydroxide and potassium nitrate was used as a sample.

When nitric acid was used, ruthenium tetraoxide was easily obtained in 95 per cent yield. The addition of sulphuric acid to nitric acid hardly influenced the yield. When acetic acid or trifluoroacetic acid was used, 30–40 per cent of the activity was measured in the mother liquor and the yield of ruthenium tetraoxide was 50–60 per cent. The addition of sulphuric or phosphoric acid to these acids, however, improved the yield to 91–97 per cent. In the case of phosphoric acid the yield reached 95–97 per cent because its dissociation constant was much smaller than that of sulphuric acid and therefore

---

(1) D. N. Hume, *Radiochemical Studies: The Fission Products* (Edited by C. D. Coryell and N. Sugarman) NNES, Plutonium Project Record, Div. IV, Vol. 9, pp. 1557–1560. McGraw-Hill, New York (1951).

(2) N. Saito *et al.*, Proceedings of the Second United Nations Conference on the Peaceful Uses of Atomic Energy, Geneva, **20**, 216–217 (1958).

(3) T. Kanbara, *Japan Analyst* **7**, 89–93 (1958).

(4) T. Kanbara, *Japan Analyst* **7**, 439–441 (1958).

it decomposed the potassium permanganate more slowly. When a mixture of silicofluoric and phosphoric acids was used, ruthenium tetraoxide was obtained in good yield, although the deposition of white hydrated silica was observed in the cooler.

In the case of the macroscale distillation with these volatile acids, the use of volatile acids prevented the precipitation of a black compound of ruthenium in the condenser.

In every case, a solution of ruthenium tetraoxide in carbon tetrachloride was easily obtained by the extraction of the distillate with carbon tetrachloride.

An example of the constitution of the reaction mixture and the yield is as follows:

CONSTITUTION OF REACTION MIXTURE

^{106}Ru-^{106}Rh (0.1 N HNO_3 soln.)	10 ml (~500,000 counts/min)
$KMnO_4$	1 g
H_2O	45 ml
CH_3COOH (purified)	30 ml
H_3PO_4 (85% soln.)	15 ml

YIELD OF ^{106}Ru

Volatile acid	Non-volatile acid	^{106}Ru used counts/min	^{106}Ru distilled counts/min	Yield (%)	Scale
	H_2SO_4	8970	6020	67	C.F.*
CCl_3COOH	–	514,000	292,000	57	C.F.
CF_3COOH	H_3PO_4	514 000	499,000	97	C.F.
CH_3COOH	–	514 000	298 000	58	C.F.
CH_3COOH	H_2SO_4	514,000	469 000	91	C.F.
CH_3COOH	H_3PO_4	514,000	497 000	97	C.F.
CH_3COOH	H_3PO_4	257 000	244 000	95	100 mg Ru
HNO_3		514 000	504 000	98	C.F.
HNO_3	H_2SO_4	514 000	487,000	95	C.F.
H_2SiF_6	H_3PO_4	514 000	509 000	99	C.F.

* C.F. = carrier-free

DISCUSSION

Ruthenium tetraoxide is a weak acid and it dissociates very slightly in its aqueous solution. F. S. MARTIN(1) reported that the first order dissociation constant was $6.8 \pm 0.3 \times 10^{-12}$. The ionized ruthenate ion reacts as a strong oxidizing agent, and decomposes into a black precipitate.

In an acid solution, the dissociation of ruthenium tetraoxide is depressed by the common ion effect and the stability of the tetraoxide increases. Therefore the yield of ruthenium tetraoxide is improved by distillation with a volatile acid which is not a reducing agent.

The well-known method of distilling ruthenium tetraoxide with carbon dioxide or perchloric acid may also be based on the same principle.

YOSHIO KODA

Government Industrial Research Institute,
Hirate-machi, Kita-ku, Nagoya Japan

(1) F. S. MARTIN, *J. Chem. Soc.* 2564-70 (1954).

Absorption spectra and configuration of the ammine complexes of copper(II)

(*Received 6 November* 1962)

In a recent paper(1) in this journal GRANT and KOLLRACK have computed the spectra of copper(II)-ammine ions from the monammine to the tetrammine by resolving the spectra of equilibrium solutions using the formation constants determined by BJERRUM. As early as 1932 such a complete analysis was made by BJERRUM(2) and the results quoted in this paper were later discussed by BJERRUM, BALLHAUSEN and JORGENSEN(3). It is however completely inexplicable that GRANT and KOLLRACK compare (in Table 2) their experimental values for the maxima of the ammine spectra in some cases

(1) D. M. GRANT and R. KOLLRACK, *J. Inorg. Nucl. Chem.* **23**, 25 (1961).

(2) J. BJERRUM *Danske Vidensk. Selsk. Mat.-fys. Medd.* **11**, No. 10 p. 46 (1932).

(3) J. BJERRUM, C. J. BALLHAUSEN and C. K. JORGENSEN *Acta Chem. Scand.* **8**, 1275 (1954).

with BJERRUM's experimental values and at other times (monammine and triammine) with calculated values found on the basis of the crystal field theory

In Table 1 GRANT and KOLLRACK's experimental values for the wavelength of the absorption maxima are compared with those obtained by us In addition are given values for the molar extinction coefficients of the absorption maxima ε_{max} is directly read from the curves (ref 1, Fig 2a, ref 3, Fig 4)

A closer consideration of the data in Table 1 shows that on the whole there is a good agreement between the experimental results of the two groups It is only for the triammine that there is a considerable deviation However this has probably something to do with the fact that GRANT and KOLLRACK apply BJERRUM's values for the consecutive formation constants determined in a 2 M ammonium nitrate medium at 30 C to their calculations in approximately 2 M ammonium *sulphate* at an unspecified temperature Changes in medium and temperature do not influence the relative values of the consecutive constants very much However the numerical values of the constants will be changed, and this will mainly influence the relative amount of triammine since the concentration of free ammonia is not negligible for $n \sim 3$

CRYSTAL FIELD CALCULATIONS

In their paper GRANT and KOLLRACK[1] postulate that according to the crystal field theory the wave number of the spectral peak of *trans* $Cu(NH_3)_2(H_2O)_2^{2+}$ should fall exactly between that of $Cu(H_2O)_4^{2+}$ and $Cu(NH_3)_4^{2+}$ assuming that the dipole moments and bond distances remain constant in each copper complex *This is an incorrect statement, and it is difficult to understand how the authors arrive at this result* considering that it is the *cis* and not the *trans* compound which has the two identical H_2O NH_3 axis According to the theory it is the sum of the contributions along each axis which alone determines the perturbation energy[5] and this leads to the opposite result, it is the wave number of the *cis* complex which under the given assumptions should be the average of that of the aquo and the tetrammine ions

In the last column of Table 1 our values for the wavelengths of the maxima of the intermediate ammine ions as calculated by BALLHAUSEN[4] are given and it is obvious that the maximum found for the diammine complex corresponds to the *cis* complex It may further be seen that a weak shoulder found in BJERRUM's curve for the diammine complex was close to the calculated value found for the *trans* complex This gives some evidence of the presence of the *trans* isomer For purely statistical reasons the concentration of the *cis* complex should be twice that of the *trans* complex, but the *cis*-*trans* ratio seems to be essentially higher than two in this case

TABLE 1 MAXIMA OF PRINCIPLE ABSORPTION PEAK FOR THE AMMINE COMPLEXES OF COPPER(II)

Copper(II) ion	GRANT and KOLLRACK		BALLHAUSEN and JORGENSEN		
	λ (mμ)	ε_{max}	λ(mμ)	ε_{max}	λ (mμ)calc
Aquo	800	13 5	790	13	–
Monammine	752	22	745	22	710
Diammine	678	30	680	29	670(*cis*)
			~600(shoulder)		620(*trans*)
Triammine	621	48	645	41	660
Tetrammine	581	52	590	53 5	
Pentammine			640	84	

GRANT and KOLLRACK assume that a statement of MELLOR[6] supports their assumption that the *trans* complex is more stable than the *cis* complex This is a wrong interpretation What MELLOR has stated in his review article in 1943 is only that solid *cis* square planar unidentate complexes of copper(II) are rarely found

J BJERRUM

Department of Inorganic Chemistry
The H C Ørsted Institute
University of Copenhagen
Copenhagen Denmark

---

[4] C J BALLHAUSEN *Introduction to Ligand Field Theory* p 106 McGraw-Hill New York (1962)

[5] C J BALLHAUSEN, *Danske Vidensk Selsk , Mat -fys Medd* **29,** No 4, p 16 (1954)

[6] D P MELLOR, *Chem Rev* **33,** 178 (1943)

The empirical relationship between the activation of energy viscosity of liquid metals and their melting points

(*Received* 24 *October* 1962)

RECENTLY, an empirical relationship was established between the activation energy of viscosity, H_η and the melting point of the metal (1,2,3) H_η is defined by Andrade's equation (see 1,2,3)

$$\eta = a \exp (H_\eta / RT),$$

where η is the viscosity in poises, H_η is in g cal/g atom and T is in °K

The relationship was not expressed algebraically because it was desirable to obtain additional data on the high temperature branch of the curve i e , viscosity data of high melting metals The scattered data on copper(4, 6, 7) and iron(7), on which we have been depending, have now been superseded by recent and more reliable measurements of CAVALIER(8) on the same metals and also on nickel and cobalt

We believe CAVALIER's data to be more accurate than the previous measurements, because they were all made by the same investigator, are self consistent, show little scatter and because they cover a

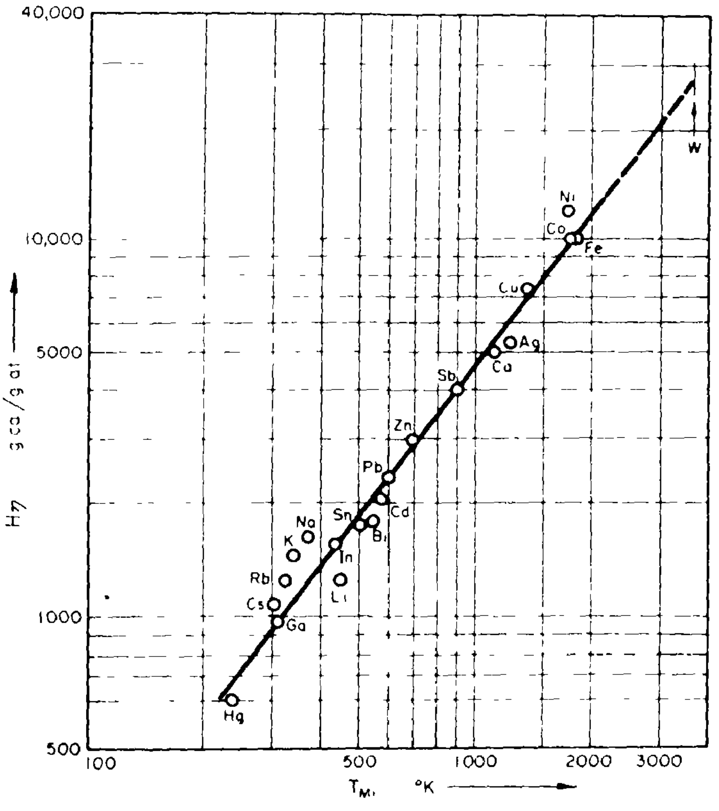


FIG. 1 Empirical relationship between H_η and T_M

A V GROSSE *The Liquid Range of Metals and some of their Physical Properties at High Temperatures*, Report of The Research Institute of Temple University Sept 5 (1960)

A V GROSSE, Paper No 2159 *A R S's Space Flight Report to the Nation*, N Y City October 9 15 (1961)

A V GROSSE *J Inorg Nucl Chem* **23**, 333 339 (1961)

A BIENIAS and F SAUERWALD, *Z anorg Chem* **161**, 51 75 (1927)

H ESSER, F FREIS and W BUNGARDT, *Arch Eisenhuttenw* **7**, 385 388 (1934)

GEBHARDT and G WORWAG, *Z Metallk* , **42**, 358 361 (1951)

N BARFIELD and J A KITCHENER *J Iron St Inst* , **180**, 324 329 (1955)

CAVALIER, *The Physical Chemistry of Metallic Solutions and Intermetallic Compounds*, Vol II, 63, Chemical Publishing, New York (1960) larger temperature interval (of about 400 K). CAVALIER's data are given in Table 1 and compared with our previous values (see Table 1 of reference 3). The new values are twice as high and therefore our empirical curve requires a revision.

Additional H_η-data[8] used are 5100 for Ca (T_M = 1123 K) and 5300 for Ag (T_M = 1233 K). For Sb an average of Cavalier's value[8] and a value from recalculated Second Liquid Metal Handbook's data was taken: H_η = 4600, T_M = 903 K. The rest of the values used are identical with those given in Table 1 of reference 3.

Based on the new data the empirical relationship is simplified. The log of H_η is a simple straight line function of the log of T_M as shown in Fig. 1 in contrast to the old curve (see Fig. 2 of ref. 3 or Fig. 11 in ref. 1).

Expressed algebraically the relationship is

$$\log_{10} H_\eta = 1.348 \log_{10} T_M - 0.366,$$

an equivalent from is

$$H_\eta = 0.431\, T_M^{1.348}$$

where T_M is the melting point of the metal in °K.

TABLE 1. VISCOSITY CONSTANTS H_η AND a OF ANDRADE'S VISCOSITY EQUATION FROM CAVALIER'S DATA[8]

Metal	T_M (°K)	η in cP (T_M)	Constant a (P × 10^3)	H_η (cal/g atom)	Old H_η values[1, 2, 3]
Cu	1357	4.09	2.58	7450	3680
Ni	1728	5.55	1.69	12000	
Co	1768	5.25	3.04	10300	
Fe	1812	5.84	3.49	10200	5070

The viscosity of *any metal at any temperature* can thus be calculated by the use of the above equations and in conjunction with the well-known Andrade equation (see refs. 1, 2, 3) for the viscosity of a metal at its melting point.

It is obvious that additional experimental measurements of the viscosity of metals melting above 1000 K, and particularly those melting above 2000 K, are highly desirable to further strengthen the empirical basis of the relationship.

Our previous estimate of the viscosity of liquid plutonium[9] requires revision. The new estimated value of H_η is 4350 instead of the old value of 3200; the new estimated value at 2000 K is 1.48 cP, instead of the value[9] of 1.72 cP (see also Table 2 of ref. 3).

A similar revision has to be made of the H_η of the lanthanide metals.[9]

Acknowledgement—The author is grateful to Mr. M. Jones of the Miamisburg Laboratories of Monsanto Chemical Company for drawing our attention to Cavalier's measurements. This work was supported in part by the U.S. Atomic Energy Commission under Contract AT(30-1)-2082.

A. V. GROSSE

Research Institute of
Temple University
Philadelphia, Pa.

[9] A. V. GROSSE, *J. Inorg. Nucl. Chem.* (1962) In Press.

The preparation of ^{210}Bi by a Szilard-Chalmers reaction

(*Received* 18 *October* 1961)

MAURER and RAMM,[1] and MURIN and NEFEDOV[2] reported the separation of ^{210}Bi from neutron irradiated organo-bismuth compounds by a Szilard-Chalmers process. In both cases carrier bismuth was added to aid the isolation of the ^{210}Bi, consequently no enrichment factors were quoted. The enrichment factors obtained in separated "carrier-free" ^{210}Bi from irradiated triphenyl bismuth and triphenyl bismuth dichloride have been determined and are reported in this note.

The results show that the highest specific activity ^{210}Bi was that separated from very pure triphenyl bismuth. The yields of ^{210}Bi were low and somewhat variable.

[1] W. MAURER and W. RAMM, *Z. Phys.* **119**, 602 (1942).
[2] A. N. MURIN and V. D. NEFEDOV, *Chem. Abs.* **50**, 3915h (1956).

EXPERIMENTAL

Triphenyl bismuth was dissolved in benzene and the solution extracted with water to remove hydrophilic bismuth impurities. The triphenyl bismuth was then twice recrystallized from benzene. Triphenyl bismuth dichloride was prepared by a standard method(5) and was recrystallized from 50/50VV chloroform methanol.

The organo-metallic compounds were sealed in small polythene bags and irradiated in BEPO at Harwell, usually for 2 hr at a flux of 2 × 10^9 neutrons cm^{-2} sec^{-1}. Varying the time of the neutron irradiation between 1 and 24 hr caused no deterioration in the performance of the solvent extraction process described below.

TABLE 1.—YIELDS AND ENRICHMENT FACTORS (E.F.) BY SOLVENT EXTRACTION SEPARATIONS

Triphenyl bismuth		Recrystallized Triphenyl bismuth		Recrystallized Triphenyl bismuth dichloride		Aqueous phase
(%) Yield	E.F.	(%) Yield	E.F.	(%) Yield	E.F.	
19	70	13*	200	14	140	a
49	250	26	430	29	very low	b
		35*	840			c
9	190	6	450			c
		7	520			c
		11	500			d
36	80					e
43	270					f
33	400					f
34	400					g

* The experiments were also carried out in presence of 0.5 mg of bismuth carrier added to the aqueous extracting phase. Recoveries of ^{210}Bi were approximately 80 per cent.

TABLE 2.—YIELDS AND ENRICHMENT FACTORS (E.F.) BY ZINC REDUCTION COLUMN METHOD

Triphenyl bismuth		Recrystallized triphenyl bismuth		Recrystallized triphenyl bismuth dichloride	
Yield (%)	E.F.	Yield (%)	E.F.	Yield (%)	E.F.
12	150	34	175	27	(low)
9	190	25	(low)		
23	165	20	500		
		23	465		

The two separation methods used in this work were solvent extraction and retention on a zinc reductor column. In the first method a weighed portion of the irradiated compound was dissolved in benzene and the solution extracted by shaking with one of various aqueous phases (see below) in a polythene ampoule. Two successive extractions were carried out. The aqueous phases were combined, backwashed with benzene and evaporated to dryness with a few drops of perchloric acid. Bismuth was isolated from the residue by quantitative extraction into carbon tetrachloride of the diethyldithiocarbamate complex(6). The amount of bismuth extracted was then determined spectrophotometrically. The carbon tetrachloride solution of the complex was evaporated to dryness and decomposed by nitric acid. ^{210}Bi was then β-counted through a 7 mg cm^{-2} aluminium absorber using a General Electric Company 2B2 Geiger Muller counter. By direct counting a weighed amount of the irradiated starting material the specific activity of the ^{210}Bi produced could be compared with the the activity of the enriched ^{210}Bi (Table 1). The aqueous phases used for the solvent extractions were (a) distilled water, (b) lanthanum nitrate solution 1 mg/ml, pH ~ 5, (c) 2% ammoniacal disodium ethylenediamine tetra acetate pH 10, (d) 2% potassium iodide pH ~ 4, (e) 5% antimonyl potassium tartrate pH ~ 5, (f) 2% ammonium oxalate, pH ~ 7, (g) disodium hydrogen phosphate and citric acid buffer pH 6.0. These reagents were chosen because it was thought that (b) and (e) might act as non-isotopic carriers and (c), (d) and (f) might act as complexing agents, while the function of (g) was primarily to act as buffer.

---

(5) Wittig and K. Clauss, *Ann.* **578**, 136 (1952).

(6) L. Cheng, R. H. Bray and S. W. Melsted, *Analyt. Chem.* **27**, 24 (1955).

Reduction separations (Table 2) were performed based on the assumption that zinc would electrochemically reduce bismuth species in solution and that the bismuth metal so formed would be deposited on the surface of the zinc metal. A benzene solution of the irradiated bismuth compound was passed through a column of zinc dust and the column then washed with several portions of benzene. The zinc was dissolved in nitric acid and the solution evaporated to dryness. The residue was dissolved in 0.5 M HCl, 1 mg of copper carrier added and then cupric sulphide precipitated. Bismuth was then extracted as the diethyldithiocarbamate, as previously described, from the mixed copper-bismuth solution.

RESULTS

In spite of the variable yields and enrichments obtained the best method discovered of preparing enriched ^{210}Bi was from irradiated pure triphenyl bismuth using as aqueous extractant ammoniacal 2% disodium ethylenediamine tetra-acetate.

D. S. POPPLEWELL

Bldg. B8.1
Atomic Weapons Research Establishment,
Aldermaston, Berks.

Homogeneous precipitation and X-ray diffraction studies of urea uranate

(*Received* 12 *July* 1962)

GENTILE, TALLEY and COLLOPY(1) first reported that urea uranate ($H_2O \cdot UO_3 \cdot 2$urea) may be obtained by simple addition of ammonium hydroxide to the water solution of uranyl nitrate and urea. The authors also reported the X-ray data of powder photographs without, however, attempting to index the reflections. More detailed studies of reactions in the system $H_2O-NH_4OH-UO_2(NO_3)_2-NH_2CONH_2$ were made by some of us(2) by means of potentiometric titrations.

We now report that urea uranate may be obtained also by homogeneous precipitation from the system $H_2O-NH_4OH-UO_2(NO_3)_2-NH_2CONH_2$. Such a method of precipitating uranium-bearing compounds has been previously reported by HERMANS(3). He did not identify the products as urea uranate, but as a nonstoichiometric compound containing 1% of urea and 9% of NH_4HCO_3. Our applied precipitation conditions were similar to those employed by Hermans except that the uranium concentration was about 50 per cent higher and no excess of nitrate was added.

The chemical analyses have shown the composition close to that expected for urea uranate $H_2UO_4 \cdot (NH_2CONH_2)_2$. The analytical procedure was the same as already described.(2)

The preliminary X-ray identification was done by means of a 57.3 mm diameter camera and CoK radiation. The data from X-ray powder patterns are shown in Table 1. For comparison, data for the samples precipitated at room temperature are included.

Further powder photographs of the samples obtained by homogeneous precipitation were taken with a camera of 57.3 mm diameter and CuKα radiation. The diffraction patterns checked in the range $\Theta = 0$–20 with the Siemens Interferenz Goniometer. It was possible to index all the reflections on the basis of an orthorhombic cell with the following dimensions: $a = 7.33$ Å, $b = 10.12$ Å, $c = 12.10$ Å. The unit cell has a volume of 897.6 Å^3 and the theoretical density is 3.14 g/cm^3, assuming four formula units per cell. This is in good agreement with the observed pycnometric density 3.10 g/cm^3. The visually-estimated intensities of the diffraction lines, and the measured and calculated $\sin^2 \Theta$ values are given in Table 2, together with the reflection indices. The conditions limiting all reflections are $(0kl)$, $k + l = 2n$, $(h0l)$, $l + h = 2n$, $h = 2n$, $(h00)$, $h = 2n$, $(0k0)$, $k = 2n$, $(00l)$, $l = 2n$, the space group is consequently Pnna D_{2h}^6. The general position of Pnna D_{2h}^6 is eight-fold and there are four sets of four-fold positions. As there are only four U atoms in the cell,

---

(1) P. S. GENTILE, L. H. TALLEY, T. J. COLLOPY, *J. Inorg. Nucl. Chem.* **10,** 110 (1958).

(2) W. DEMBINSKI, A. DEPTULA, *Nukleonika,* **7,** 325 (1962).

(3) M. E. HERMANS, *Proc. Second Geneva Conf. Peaceful Uses of Atomic Energy,* paper 552 (1958).

TABLE 1 — THE d_{hkl} (Å) VALUES FROM THE UREA URANATE POWDER PATTERNS

$H^{(a)}$	exp $4^{(b)}$	exp $6^{(c)}$	GENTIL'S data d	GENTIL'S data I/I_0
7 78$_3$	7 76$_3$	7 84$_3$	7 76	100
	—	—	7 35	10d
6 09	6 02	6 09	6 03	15
5 10	5 08$_1$	5 15$_1$	5 08	40
3 90	3 90	3 92	3 91	10
3 72	3 75	3 79	3 79	15
3 66	3 65	3 66	3 66	15
3 50	3 50	3 50	3 52	10d
3 30$_2$	3 30$_2$	3 30$_2$	3 30	50d
		—	3 19	10d
3 12	3 11	3 12	3 14	10d
2 97	2 96	2 97	2 97	15

3 first intensity, d diffusion
2 second intensity,
1 third intensity lines

(a) homogeneous precipitated (analysis U, 56 01, N, 13 17, H_2O 4 47%. Expected U, 56 12 N 13 21, H_2O 4 25%)

(b) precipitated at room temperature by slow addition of 1 68 N ammonium hydroxide to a water solution containing 91 1 g U/l and 68 95 g Urea/l (analysis U, 55 98, N, 13 10, H_2O, 4 64%)

(c) as above (b) but urea concentration in the starting solution 184 68 g Urea/l (analysis U, 56 28 N 12 92, H_2O, 4 67%)

TABLE 2

I/I_0	hkl	$\sin^2$ (obs)	$\sin^2$ (cal)
vs	011	0098	0098
m	002	0162	0162
s	020	0231	0232
w	022	0395	0394
w	013	0424	0423
m	200	0449	0446
s	211	0548	0548
s	031	0560	0562
w	202	0610	0608
w	220	0680	0678
vvw	222	0843	0840
vw	213	0872	0868
m	040	0925	0928
vw	231	1010	1008
vw	042	1087	1090
vw	303	1367	1367
vvw	051	1492	1491
vvw	135	1649	1646
vw	400	1782	1782
m	411	1879	1881
vvw	153	1926	1926
vvw	305	2016	2016
vw	422	2179	2177
vvw	414	2489	2489
vvw	501	2828	2826
w	171	2994	2994
m	406	3242	3241
vw	436	3762	3763
vvw	612	4230	4230
vvw	456	4690	4690

they must lie on four-fold positions. Taking into account only the stronger reflections, the following additional limiting conditions are obtained (hkl) $h + k + l = 2n$, $h = 2n$, $k + l = 2n$. This indicates that the uranium atoms lie at a position with the point symmetry $\bar{1}$ or 2-(Wyckoff notation *a*, *b* or *c*).

Acknowledgements. The authors wish to thank MRS Z. SZMID from the Institute of Nuclear Research, Warsaw and MR A. URBANC from "Jozef Stefan" Institute Ljubljana for preparing the X-ray patterns.

Institute of of Nuclear Research, Warsaw
Nuclear Institute "Jozef Stefan", Ljubljana

W. DEMBINSKI*
A. DEPTULA
B. VOLAVSEK

* Under the IAEA fellowship at Nuclear Institute "Jožef Stefan" Ljubljana

---

New polymeric sulphur nitrides

(*Received* 9 *October* 1962, *in revised form* 28 *November* 1962)

FROM several unsuccessful attempts to prepare the double ring compound bis-heptasulphur imidyl by the reaction

$$Hg(S\text{-}N)_2 + I_2 \rightarrow HgI_2 + (S\text{-}N)_2$$

have obtained instead a mixture of sulphur-nitrogen polymers.

Bis-heptasulphur imido mercury was prepared from 99 per cent pure heptasulphur imide by a published method.[1] It was, however, filtered under nitrogen, washed with anhydrous methanol and dried quickly in a stream of nitrogen in place of the procedure described in this reference. In the most fully investigated run 1.92 m mole of the mercury compound was suspended in 5 ml of pure carbon disulphide under nitrogen. 1.92 m mole of iodine in 10 ml of the same solvent was added at 0° with shaking. The iodine colour disappeared and 1.80 m mole of mercury (II) iodide was precipitated. The orange-red solution was concentrated and put through a column of chromatographic silica gel 27 cm × 3.8 cm, eluting with carbon disulphide. The eluted substances consisted of polymer R_f from 1.00 to about 0.60, total weight 0.913 gm, and tetrasulphur tetranitride in two portions, 0.016 m mole at R_f = 0.6 and 0.033 m mole at R_f = 0.14. There was also 0.22 m mole of heptasulphur imide at R_f = 0.55; this may have come from the hydrolysis, during subsequent handling, of a little unreacted bis-heptasulphur imido mercury. (S_4N_4 and S_7NH were identified and quantitatively determined by IR.)

The polymer was a red, transparent, viscous liquid with the consistency of soft pitch, unaffected by air or water. All fractions had mol. wt. between 2400 and 3400 (by lowering of the vapour pressure of carbon disulphide). The fractions with R_f near 1 comprised the bulk of the material, and had the empirical composition $S_{10}N$. Their only IR absorptions between 2.5 and 15 μ were overlapping bands at 12.9 (strong), and 12.4 and 13.5 μ (medium). The fractions with R_f = 0.7 had the empirical composition $S_{11.5}N$ and the same three IR absorptions, but with the 12.9 μ band about half as strong. Most of the polymer material was extremely soluble in carbon disulphide but almost insoluble in other common solvents. The fraction with R_f = 1, for instance, had solubility = 234 g/100 g carbon disulphide. In 94 mole per cent carbon disulphide, 6 mole per cent carbon tetrachloride the solubility was only about 7 g/100 g solvent.

Three months after preparation, crystals of rhombic sulphur had formed in the polymer, especially in the fractions R_f = 0.60–0.79. The average mol. wt. of the fraction R_f = 0.79 had fallen from 2600 to 1300. The IR was little changed.

The polymer may have originated from decomposition of S-N radicals, which were probably the primary reaction product; an S-N radical might well be able to attack another S-N ring at any point. Alternatively, the double ring compound may have formed and then decomposed; this compound is likely to be much less stable than heptasulphur imide, since the canonical forms with charged nitrogen, which contribute to the considerable resonance stabilization of the imide[2], are forbidden in the double ring compound by the adjacent charge rule. The breakdown of either or both of these substances could give rise to complex structures with sulphur chains of various lengths, linked and cross-linked through nitrogen atoms, and perhaps terminated by S-N rings, and also to the tetrasulphur tetranitride found. The fraction of the latter with R_f = 0.6 must have been formed during elution by the decomposition of some compound with $R_f \sim 1$.

The three IR bands of the polymer are probably all stretching modes of S–N bonds in different environments.

We hope to learn more about the structure of the polymer from experiments now in progress on controlled hydrogenolysis.

Chemistry Department
Queen's University, Belfast

J. BUCKLEY
H. G. HEAL

---

[1] A. MEUWSEN and F. SCHLOSSNAGEL, *Z. anorg. Chem.* **271**, 226 (1953).

[2] M. GOEHRING, *Ergebnisse und Probleme der Chemie der Schwefelstickstoffverbindungen* p. 58. Akademie, Berlin (1957).

The reaction of gallium dichloride with water and hydrogen sulphide

(*Received* 5 *December* 1962)

The hydrolysis product of gallium dichloride

It has previously been reported[1] that solutions of gallium dihalides in benzene are very prone to attack by even minute traces of moisture; a brown hydrolysis product is first precipitated and, if more than a trace of water is present, the brown precipitate reduces the excess water to hydrogen

---

[1] S. M. ALI, F. M. BREWER, J. CHADWICK and G. GARTON, *J. Inorg. Nucl. Chem.* **9**, 124 (1959).

The affinity for water is so great that the hydrolysis product is precipitated rather than the coordination complex if a ligand solution containing a trace of water is added to a benzene solution of a gallium dihalide

Investigation of the brown hydrolysis product of gallium dichloride has yielded some information, although the exact nature of the compound is still uncertain

Preparation of the brown hydrolysis product of gallium dichloride

The hydrolysis product was precipitated by adding undried benzene to a solution of gallium dichloride in dry benzene under a nitrogen atmosphere as described for the preparation of Ga_2Cl_4 complexes in a previous communication[1] The brown precipitate was filtered, washed with dry benzene, dried in a current of dry nitrogen and left overnight in a vacuum desiccator to remove the last traces of benzene

Quantitative analysis of the powder showed a Ga Cl ratio of 1 1 (Anal found Ga 52 95 Cl, 27 5% Ga Cl 1 1 02) (The substance contained no carbon) The mean valency of the gallium in the compound was shown to be 2, by reaction with acidified standard potassium permanganate

When the brown hydrolysis product was heated to about 100 C under reduced pressure (10^{-3} mm Hg) water was evolved and the colour of the powder changed from brown to creamy white Analysis of the white powder again showed a 1 1 Ga Cl ratio and the mean valency of the gallium was again shown to be 2 The weight loss after evolution of the gas indicated the removal of half a molecule of water per gallium atom

$$GaClX\,\tfrac{1}{2}H_2O \quad GaClX \quad \tfrac{1}{2}H_2O$$

(where X the residue after estimation of Ga, Cl and readily removable H_2O)

The analyses of the brown hydrolysis product and its white derivative can be explained only by assuming that the residue X is O, OH or H_2O, of which only OH satisfies the valency requirement The analyses for the two compounds are

$GaCl(OH)\,\frac{1}{2}H_2O$				$GaCl(OH)$	
	Theory (%)	Found (%)		Theory (%)	Found (%)
Ga	53 1	52 95	Ga	57 1	57 3
Cl	27 1	27 5	Cl	29 0	29 15
OH H_2O*	19 8	19 6	OH*	13 9	13 5

* By difference

No solvent was found which would dissolve either of these compounds without decomposing them therefore no conductivity or cryoscopic measurements could be made

The thiohydrolysis product of gallium dichloride

A white precipitate was formed by passing dry H_2S into a solution of gallium dichloride in benzene There was no evolution of hydrogen and no brown hydrolysis product was formed The precipitate was collected and washed with dry benzene, excess benzene was then removed by a stream of dry nitrogen and last traces *in vacuo*

Analysis of the precipitate showed it to have the composition GaClY (where Y S SH or H_2S of which only SH appears likely) (Anal Found Ga, 50 3 Cl, 25 2 S 23 1% GaClSH requires Ga 50 4 Cl 25 6, S 23 2%) S was determined as $BaSO_4$ after oxidation with fuming nitric acid

The compound was strongly reducing A known weight of the substance was added to an excess of acidified standard iodine solution Sulphur was precipitated by oxidation of sulphide ion therefore the mixture was shaken for some time to ensure complete reaction Excess iodine was back-titrated with standard sodium thiosulphate solution 2 92 equivalents of iodine were reduced per g atom of Ga in the compound Deducting 2 equivalents for oxidation of sulphide ion ($S^{=}$ I_2 → S↓ $2I^-$) 0 92 equivalents of iodine were reduced per Ga atom The mean valency of Ga in the compound was 2 08 i e 2 allowing for slight oxidation on handling

Cryoscopic or conductivity measurements were not made because again no suitable solvent could be found

DISCUSSION

Without the benefit of cryoscopic or conductivity measurements, any discussion of the structure of these compounds must be hypothetical. However, it appears reasonable to assume that the thiohydrolysis product GaClY and the white derivative of the hydrolysis product, GaClX, possess similar structures.

The mean valency determinations demonstrate that both compounds contain equal numbers of Ga(I) and Ga(III) atoms. It is possible that these compounds have structures based on the structure of the parent compound, gallium dichloride, with discrete anions and cations Ga(I)$^+$ and Ga(III)Cl_2(X or Y)$_2^-$, but they could also contain polymeric anions.

Carlston *et al.*[illegible] have reported a white precipitate which is formed by the action of H_2S on gallium dihalides. These authors were, however, unable to obtain precipitates of constant composition. They imply that their results indicate the formation of an entirely monovalent gallium compound, but we suggest that a mixed-valence compound analogous to the hydrolysis product is actually formed.

The Inorganic Chemistry Laboratory
Oxford

F. M. Brewer
J. R. Chadwick*
G. Garton†

* Now at Northampton College of Advanced Technology, London.

† Now at the Clarendon Laboratory, Oxford.

[illegible] R. C. Carlston, E. Griswold and J. Kleinberg, *J. Amer. Chem. Soc.* **80**, 1535 (1958).

Reactions of HCl and HF with Ga_2Cl_4

(*Received 18 October 1962; in revised form 5 December 1962*)

Although many complex halides of the type $M_n(AX_n)$, where M is a metal ion and X a halogen, have been described previously, reports concerning the corresponding complex acids, $H_n(AX_n)$, are considerably fewer. The existence of a complex acid in solution has often been inferred from physical or chemical data. Moreover, complex acids have been proposed as intermediates in reactions such as the Friedel-Crafts reaction.

In a study of the distribution of gallium trichloride between ether and aqueous hydrochloric acid solutions, Nachtrieb and Fryxell[1] reported the presence of $HGaCl_4$ in the ethereal phase. Wiberg, Schmidt and Galinos[2] subsequently isolated complex halogen acids of the type $HMX_4 \cdot 2R_2O$ where M = Al, Ga, In, Tl and X = Cl, Br. Recently Galinos[3] reported the preparation of etherated mixed halogen acids of Group IIB and IIIB metals.

Although an extensive series of stable complex gallic fluorides is known[4-7] the corresponding complex acid H_3GaF_6 has not previously been described.

In the present work hexafluogallic and dioxanated tetrachlorogallic acids have been isolated as white crystalline powders.

Preparation of reagents

Gallium (I) tetrachlorogallate (III) (gallium dichloride) was prepared[8] and dioxan was dried[9] by the methods previously described.

[1] N. H. Nachtrieb and R. E. Fryxell, *J. Amer. Chem. Soc.* **71**, 4035 (1949).

[2] E. Wiberg, M. Schmidt and A. G. Galinos, *Angew. Chem.* **66**, 443 (1954).

[3] A. G. Galinos, *J. Amer. Chem. Soc.* **82**, 3032 (1960).

[4] O. Hannebohn and W. Klemm, *Z. anorg. Chem.* **229**, 341 (1936).

[5] W. Pugh, *J. Chem. Soc.* 1046 (1937).

[6] W. Pugh, *J. Chem. Soc.* 1959 (1937).

[7] E. Einecke, *Angew. Chem.* **55**, 40 (1942).

[8] G. Garton and H. M. Powell, *J. Inorg. Nucl. Chem.* **4**, 84 (1957).

[9] S. M. Ali, F. M. Brewer, J. Chadwick and G. Garton, *J. Inorg. Nucl. Chem.* **9**, 124 (1959).

Reaction of gallium (I) tetrachlorogallate (III) with hydrogen chloride

Dry hydrogen chloride was passed through a solution of gallium (I) tetrachlorogallate in dioxan Hydrogen was evolved and after about 10 min the solution separated into two layers With further passage of hydrogen chloride, the volume of the denser phase increased until the two layers suddenly merged to form a homogeneous solution, which, although showing no further visible change continued to absorb hydrogen chloride Dry, oxygen-free nitrogen was passed through this solution to remove excess hydrogen chloride, when an equally sudden redivision into two layers occurred Neither of the two liquid phases showed the strong reducing properties characteristic of gallium (I)

Examination of the light phase

Evaporation of this liquid under reduced pressure yielded very deliquescent crystals of $GaCl_3$ 2 diox (diox 1,4-dioxan) (Anal Found Ga, 19 8 Cl, 30 3 $GaCl_3$ 2 diox requires Ga, 19 8 Cl, 30 2%)

Examination of the dense phase

Nitrogen was passed through the liquid for several hours, after which the deliquescent white solid $HGaCl_4$ 3 diox was deposited, this was filtered off washed with dry ether and the excess solvent removed *in vacuo* (Anal found Ga, 14 6 Cl, 29 7 $HGaCl_4$ 3 diox requires Ga, 14 6, Cl 29 7%) m p 123 dec

Estimation of the hydrogen evolved

The hydrogen evolved during reaction of HCl gas with a known weight of gallium (I) tetrachlorogallate, was determined quantitatively as H_2O Duplicate determinations were carried out Results Weight H_2O found (i) 0 0450 (ii) 0 0463 g Weight H_2O calculated for the oxidation of Ga(I) to Ga(III), 0 0462 g

NH_4GaCl_4 Dioxan

A solution of tetrachlorogallic acid in dioxan was treated with a dioxan solution of ammonium thiocyanate, when a white precipitate was immediately formed This was washed by decantation with dry dioxan and excess solvent removed *in vacuo* (Anal found N, 4 5 Ga, 21 8 Cl, 44 4 NH_4GaCl_4 diox requires N, 4 3, Ga, 22 0, Cl, 44 7%)

On heating the compound lost dioxan at 120 C and subsequently melted in the range 275–285 C which is somewhat lower than the melting point of 305 C recorded by FRIEDMANN and TAUBE[10]

NH_4GaCl_4 Diox was also precipitated by mixing dioxan solutions of gallium (I) tetrachlorogallate and ammonium thiocyanate

Reaction of gallium (I) tetrachlorogallate (III) with hydrogen fluoride

When dry hydrogen fluoride was passed into a dioxan solution of gallium (I) tetrachlorogallate hydrogen was evolved and a fine white precipitate of GaF_3 diox was immediately formed (Anal found Ga, 32 3, F, 26 3 GaF_3 diox requires Ga 32 5 F 26 5%)

This compound was thermally stable up to 300 C but at higher temperatures gave off dioxan and then remained apparently unchanged up to bright red heat The residue was GaF_3 (Anal found Ga, 54 9 F, 44 6, GaF_3 requires Ga 55 0, F 45 0%)

The liquid remaining after precipitation of GaF_3 diox was treated with an equal volume of diethyl ether to give a dense white precipitate of H_3GaF_6 (Anal found Ga 37 6 F 60 8 H_3GaF_6 requires Ga 37 3 F 61 1%)

Analytical methods

Determinations of gallium and fluoride in the compounds containing these elements were carried out by a method described previously[11] Nitrogen was determined by Kjeldahl's method and chloride by Volhard's method

Discussion

Gallium (I) tetrachlorogallate (III), $Ga^I(Ga^{III}Cl_4)$ dissolves in dry dioxan to give $Ga(diox)_2^+$ $GaCl_4^-$, which has been described previously[8] Hydrogen chloride dissolves in dry ethers to form

---

H L FRIEDMAN and H TAUBE *J Amer Chem Soc* **72**, 2236 (1950)

M BREWER, G GARTON and D M L GOODGAME, *J Inorg Nucl Chem* **9**, 56 (1959) the corresponding oxonium compounds Thus solutions of Ga(GaCl$_4$) and hydrogen chloride in dry dioxan probably contain the dioxanated ions or ion-pairs

$$(\text{diox})\,\text{H} \qquad \text{Cl} \qquad (\text{diox})_2\text{Ga} \qquad (\text{GaCl}_4) \tag{1}$$

The separation of the dioxan solution into two phases resembles in this respect concentrated solutions of the compounds NH$_4$MCl$_4$ (M Fe Al Ga) and lithium tetrachlorogallate in ether(12) and of gallium (I) tetrachlorogallate (III) in benzene The dioxanated complex acid H(GaCl$_4$) diox separates into the denser phase The free gallium (I) ion in the lighter phase reduces the excess hydrogen ions thus

$$\text{Ga} \qquad 2\text{H} \qquad \text{Ga} \qquad \text{H}_2 \tag{2}$$

The quantitative determination of the hydrogen evolved showed that reaction (2) was indeed taking place and that all of the monovalent gallium was oxidized to the trivalent state The isolation of the compound GaCl$_3$ 2 diox from the dioxan solution confirms this

Hexafluogallic acid prepared as described differs from those described by WIBERG *et al* (2) in having no co-ordinated ether molecules The compound H$_3$AlF$_6$ was reported by Tananaev only as tri- and hexahydrates(13)

It is not surprising that the action of hydrogen fluoride on solutions of gallium (I) tetrachlorogallate yields a complex acid containing the (GaF$_6$)^3 ion and not the (GaF$_4$) ion Whereas many complexes of the type M$_3$(GaF$_6$) have been described(1 7) no complexes of the type M(GaF$_4$) involving discrete (GaF$_4$) ions have been reported For example, NH$_4$GaF$_4$ is isomorphous with NH$_4$AlF$_4$(11) and has a structure wherein each gallium atom is surrounded by an octahedron of six fluorine atoms

The Inorganic Chemistry Laboratory
Oxford

F M BREWER
J R CHADWICK*
G GARTON†
D M L GOODGAME‡

* Now at Northampton College of Advanced Technology London

† Now at the Clarendon Laboratory Oxford

‡ Now at Imperial College London

(12) H L FRIEDMAN and H TAUBE *J Amer Chem Soc* 72, 3362 (1950)

(13) I TANANAEV *J Gen Chem Moscow* 8, 1120 (1938)

Preparation and properties of aluminum phosphide

(*Received* 28 *September* 1962 *in revised form* 12 *December* 1962)

THE PREPARATION of various aluminum phosphides was reported early from the reaction of the elements(1) Later, WHITE and BUSHEY(2) found AlP to be the only compound formed in the Al-P system AlP has been prepared by ADDAMIANO(3) by the replacement of Al with Zn$_3$P$_2$

Most of the AlP used in these studies was prepared by the replacement reaction which yields a powdered product The purity of the product was increased to better than 99 per cent by resublimation of Zn$_3$P$_2$ supplied by Fisher Scientific Company at 900 950 C and by vacuum heating the aluminum

All X-ray diffraction studies were carried out on a General Electric XRD-5 unit with spectrogoniometer using filtered CuK$_\alpha$ radiation

Calorimetric studies were carried out using an oxygen bomb calorimeter Since data are not available for the combustion products, equal molar mixtures of aluminum powder and red phosphorus were fired under the same conditions as the AlP samples The heat of formation of AlP was calculated by subtracting the heat of combustion of AlP from the heat of combustion of the mixture thereby eliminating the need for product identification

(1) F WOHLER *Pogg ann* **11**, 160 (1872), L FRANK *Chem Ztg* **22**, 237 (1898), L MOSER and A BRUHL, *Z anorg allgem Chem* **121**, 73 (1922)

(2) W L WHITE and A H BUSHEY *J Amer Chem Soc* **66**, 1666 (1944)

(3) A ADDAMIANO, *Acta Cryst* **13**, 505 (1960)

Results and discussion

AlP slowly undergoes air hydrolysis to form α-Al_2O_3 and PH_3. The freshly prepared material is pea green in colour. The colour changes to greyish white as the hydrolysis continues. The density of the powder was found to be 2.40 ± 0.01 g/cm³ using dinonyl phthalate as the pycnometric fluid while a density of 2.36 g/cm³ was calculated from X-ray data.

AlP reacts with water and dilute alkali solution with the slow evolution of PH_3 while the evolution occurs with explosive violence with dilute mineral acids. At temperatures of 700°C and above, AlP reacts with pure oxygen to form orthorhombic $AlPO_4$. AlP is thermally stable in an inert atmosphere up to about 1100°C. Above 1200°C, it decomposes to phosphorus and probably aluminum since no lower phosphides were observed.

The crystal structure of AlP is face-centered cubic (zinc blende type) with the cell parameter a_0 = 5.467 ± 0.002 Å as obtained by a least squares extrapolation of the function $(\cos^2\theta)/\theta + (\cos^2\theta)/\sin\theta$.⁽⁴⁾ Addamiano has reported a value of 5.451 ± 0.004 Å. The line intensities in the X-ray powder pattern observed in this work are in good agreement with those of Addiamiano. The interatomic distances as calculated from these data are 2.367 Å for Al-P and 3.870 Å for Al–Al.

The calorimetric studies resulted in a value of −29 ± 2 kcal/mole for the heat of formation of AlP at 25°C.

Acknowledgement. This work was supported by a grant from Texas Instruments Incorporated, Dallas, Texas.

Department of Chemistry
Colorado State University
Fort Collins, Colorado

C. C. Wang,*
M. Zaheeruddin†
Leo H. Spinar‡

* Present address: Department of Chemistry, University of Kansas, Lawrence, Kansas.
† Present address: Peshawar University, Peshawar, Pakistan.
‡ Present address: Department of Chemistry, University of Missouri, Columbia, Missouri.

⁽⁴⁾ J. B. Wilson and D. P. Riley, *Proc. Phys. Soc.* 57, 160 (1945).

J. Inorg. Nucl. Chem. 1963. Vol. 25, pp. 329 to 330. Pergamon Press Ltd. Printed in Northern Ireland

BOOK REVIEWS

Electrolytes, *Proceedings of an International Symposium held in Trieste, June* 1959. Edited by B. Pesce. 360 pp. Pergamon Press, Oxford, 1962. Price 100s.

THE TEMPTATION to publish the proceedings of specialist conferences is one which appears to be increasingly difficult to resist. Such publications are sometimes justifiable but the present volume violates most of the criteria which distinguish a satisfactory report of an International Symposium. Rapidity of publication is essential since reports loose much of their value of publication if unduly delayed. Techniques are well established for publishing the papers either simultaneously with the conference, (e.g. Proceedings of the Sixth International Symposium on Coordination Chemistry) or within a few months of its completion, (e.g. Chemical Society Symposia, Faraday Society Discussions etc.) yet this conference on Electrolytes was held over 3 years ago. As a result some of the papers have, in the mean time, been republished elsewhere.

Again publication may be justified if the lectures and the discussions arising out of them are reported in a uniform style. This book contains no discussion and the manuscripts of the 32 lectures could, presumably, have been available in June 1959. The treatment varies from extended abstracts (4 pages) to comprehensive articles (27 pages) and the topics vary from reviews to original research papers. Twenty-two of the papers are in English, six in Italian, three in German and one in French. Several of the papers by European scientists are in English and the value of the book to many readers would have been enhanced if the papers in Italian had also been translated. The general excellence of the language in those articles which have been translated makes the occasional lapse more noticeable and unfortunate phrases such as "a weighed several gram sample" and measurements "with second class electrodes" should not have slipped passed the Editor.

A third reason for publishing proceedings is to bring an unfamiliar subject of rapidly growing importance and applicability to a wider circle of readers than those who attended the conference. This Symposium was held to celebrate the centenary of the birth of Arrhenius and, whilst it is true that the eminence of many of the contributors will rightly commend the book to those interested specifically in aqueous electrolyte solutions, it is also true that the same ground has been covered by more than one volume in recent years. The price is far higher than that of many specialist monographs of similar length and this further reduces the attractiveness of the book.

It is not possible in a short review to list the titles of all the papers presented or to do justice to their contents, but some indication of the range, quality and authoritativeness of the Symposium can be gained by mentioning the names of some of the authors: these include Accascina, Debye, Eigen, Fajans, Falkenhagen, Fuoss, Guggenheim, Janz, Lange, Onsager, Robinson, Shedlovsky and Stokes.

N. N. GREENWOOD

J. H. KNOX: **Gas Chromatography,** Methuen, London 1962. v + 126 pp., 15s.

CONDENSATION of the essential features emerging from the mushrooming literature of Gas Chromatography into the pocket-sized format of the Methuen Monograph Series requires the exercise of considerable judgement and discretion. To supplement the text with the personal hints and accumulated experience of a leader of progressive techniques in this subject and to emphasize the characteristics of capillary columns and ionization detectors presents a task only to be undertaken by an enthusiast. With this well illustrated book the author succeeds in all his aims.

A short introductory chapter scans the history, development and scope of gas chromatography. Chapter 2 introduces the reader to the theory of the process and guides him as far as high performance column theory and the equations of Golay and Van Deemter. Chapter 3 presents practical details of column design and the selection of suitable supports and liquid phases. This section is no mere catalogue of materials and chemicals but carries the hall-mark of the author's wide experience throughout. The newcomer to the subject will make few errors if he adheres to the advice given here. The following chapter on detectors is a masterpiece of compression and includes details of the construction of all types of detectors, their mode of action, special fields of use and limitations. Only the thermistor receives scant attention but in compensation the katharometer is very adequately covered. A selection of suitable designs of some of the ancillary equipment, e.g. flow meters, thermostats, injection systems etc. commonly used is given in Chapter 3 which is followed by a consideration of temperature programming and preparative scale methods. A short concluding chapter contains an account of the documentation of gas chromatography. A list of symbols used and an adequate index is included.

Dr. Knox can be congratulated on this book, a most worthy addition to a distinguished series. It should reach a wide public. It is more than adequate for the Honours student and well within his financial reach. The analyst will benefit from the wealth of experience in the general background to the subject that has been condensed within its covers, whilst the research worker who thumbs his way through will be given cause to enquire whether his existing apparatus is really optimized for the job. The inorganic chemist, whilst not specifically catered for, will be stimulated by the statement of page 8 forecasting the use of this technique for the analysis of inorganic salts boiling above 1000°C.

F. S. LANE

A. B. GRINBERG: **An Introduction to the Chemistry of Complex Compounds.** Translated from the 2nd Ed. (1951) by J. R. LEACH and Edited by D. H. BUSCH and R. F. TRIMBLE. Pergamon Press, Oxford 1962. 363 pp. 105s.

THIS book is a translation of GRINBERG's *Vvedenie v Khimiyu Kompleksnykh Soedinenii*. Editorial comments are inserted in the text as footnotes. The Russian text was translated in order to acquaint chemists with the approach of the "Russian School" to coordination chemistry, as well as to provide an intermediate level textbook in this area. In the opinion of the reviewer the book is unsuitable for teaching purposes but experts in the field of coordination chemistry may find that it provides a useful survey of the essentially experimental approach to the subject favoured by Russian chemists.

By British standards the book dates to about 1950. Topics of the greatest importance which are not discussed include molecular orbital theory and crystal field theory as applied to complex compounds, and reaction mechanisms of complexes in aqueous solution. Metal carbonyls receive only very brief mention, and in view of the date of publication of the original Russian version of the book there is naturally no description of the chemistry of π-complexes. Written before the death of Stalin the book contains frequent statements having a political bias.

The book is certainly not suitable for students. From it they would obtain a very unsatisfactory account of the chemistry of complexes. Treatment of the subject is far too historical and the experimental work described far too classical. Infrared, ultraviolet and visible spectroscopy, magnetic studies, and other techniques now used to elucidate the nature of complexes, are hardly mentioned. However, from the point of view of a research worker experienced in the field of coordination chemistry, the book has some interesting sections.

The book is very attractively bound and printed, and although there are errors of a typographical nature, including one in the preface, they are relatively few in number.

F. G. A. STONE

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 331 to 334. Pergamon Press Ltd. Printed in Northern Ireland

THE DENSITIES OF LIQUID IRON AND NICKEL AND AN ESTIMATE OF THEIR CRITICAL TEMPERATURE

A. V. GROSSE and A. D. KIRSHENBAUM*
Research Institute of Temple University, Philadelphia

(*Received 2 August 1962*)

FOR the last two years experimental density determinations were made at the Institute of a number of metals from the melting point to the normal boiling point (Sn, Pb, In, Mg, Bi, U, Cu, Sb, Ag[1]). We have also shown[2,3,4,5] that the critical temperatures of metals can be estimated by two essentially independent methods, (a) from the law of rectilinear diameter, determined by the experimental densities of the liquid metal and its saturated vapour and (b) from the theorem of corresponding states, using the experimental data on liquid mercury which cover the whole liquid range from the melting to the critical point. The use of both methods is illustrated by the liquid range temperature diagrams of lead[6] and silver[6].

In the case of all metals investigated to date there is reasonable agreement between the two methods of calculating critical temperatures. We now wish to report *two exceptions*, namely liquid iron[7] and nickel[8] whose densities were also measured from the melting point to approximately the normal boiling point by both the Archimedean and maximum bubble methods with excellent agreement. The liquid densities are straight line functions of temperature and are expressed by the following equations:

$$D^{\mathrm{Fe}}_{(\mathrm{liq.})} = 8.618 - 8.83 \times 10^{-4}T$$

and

$$D^{\mathrm{Ni}}_{(\mathrm{liq.})} = 9.908 - 11.589 \times 10^{-4}T$$

---

* This work was supported by the National Science Foundation under Grant No. 18829.

[1] See various contributions by A. D. KIRSHENBAUM, J. A. CAHILL, P. J. MCGONIGAL and A. V. GROSSE in *J. Inorg. Nucl. Chem.*, *J. Phys. Chem.*, *J. Amer. Chem. Soc.* and *Trans. Quarterly of A.S.M.*

[2] A. V. GROSSE *J. Inorg. Nucl. Chem.* **22**, 23 (1961).

[3] A. V. GROSSE, The Liquid Range of Metals, and Some of their Physical Properties at High Temperatures. Paper No. 2159, A.R.S., *Space Flight Report to the Nation* New York, October 9–15 1961.

[4] A. V. GROSSE, The Liquid Range of Metals and Some of their Physical Properties at High Temperatures, Report of the Research Institute of Temple University, October 19, 1960.

[5] A. V. GROSSE, *Inorg. Chem.* **1**, 436 (1962).

[6] A. V. GROSSE and A. D. KIRSHENBAUM *J. Inorg. Nucl. Chem.* **24**, 739 (1962).

[7] A. D. KIRSHENBAUM and J. A. CAHILL, *Trans. of the Met. Soc. of AIME*, **244** (1962). Presented before the 91st Annual Meeting of the Metallurgical Society of AIME in New York City, February 20, 1962.

[8] A. D. KIRSHENBAUM and J. A. CAHILL *Trans. Quarterly of A.S.M.* In Press.

where D is in g/cm^3 and T in °K. The liquid densities at the melting and normal boiling points are as follows:

	Fe	Ni
$D_{m.p.}$ (g/cm^3)	7.015	7.905
m.p. (°K)	1805	1728
$D_{b.p.}$ (g/cm^3)	5.828	6.304
b.p. (°K)	3160	3110

The equation of the rectilinear diameter (in the same units) are as follows:

$$D_d^{Fe} = 4.309 - 4.42 \times 10^{-4}\,T$$

and

$$D_d^{Ni} = 4.954 - 5.795 \times 10^{-4}\,T$$

The liquid range diagrams of the two metals were constructed and that of iron is given in Fig. 1. The critical temperatures of Fe, estimated *at* 6750 K, and of Ni,

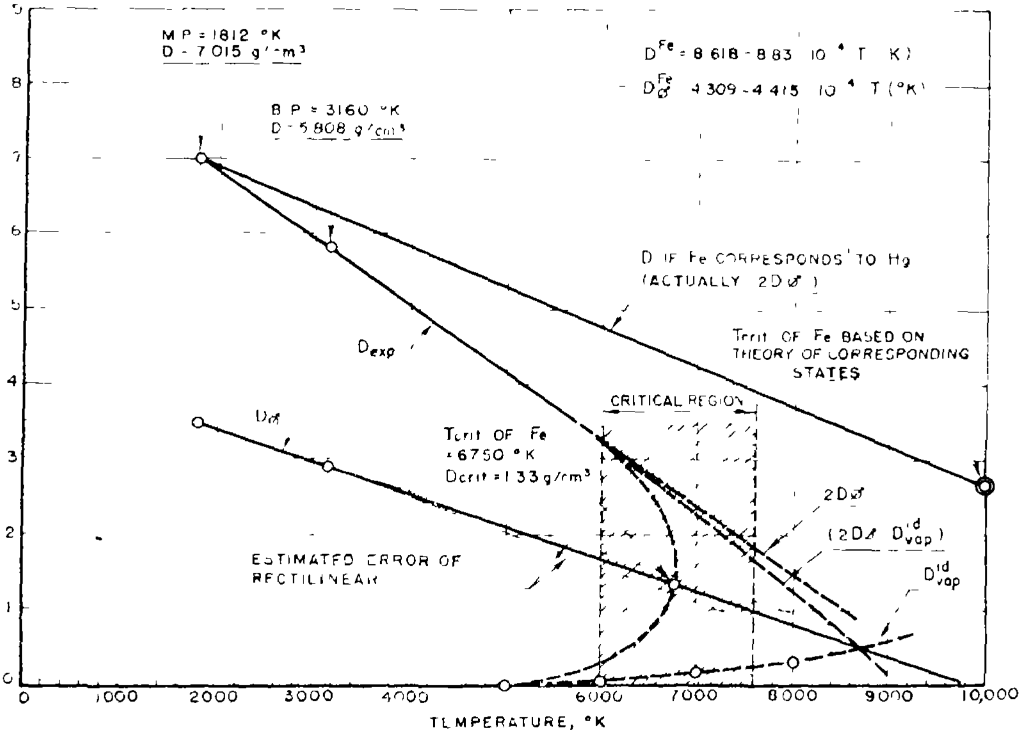


FIG. 1

estimated *at* 6000 K, were based on the ratio of $D_{b.p.}/D_{crit.p.} \sim 4.35$, since this ratio is based on the liquid range diagram of many other metals[9], i.e. Hg, Bi, Ag, Pb, Sn and Ga. However, if we base our estimates of critical temperatures on the law of corresponding states and the following reliable heats and entropies of vaporization[10] of iron and nickel:

---

[9] P. J. McGONIGAL, A. D. KIRSHENBAUM and A. V. GROSSE, *J. Phys. Chem.*, **66**, 737 (1962).

	N B P (K)	ΔH_{vap} (kcal/g atom)	ΔS (cal/g atom K)	T_{red} based on Hg	T_{crit} (K)
Fe	3160	83,900	26 7	0 31	10 000
Ni	3110	88,870	28 5	0 29	10,700

we obtain the values of 10,000 and 10,700 K for Fe and Ni respectively If these values are correct it follows since the $D_{b\ p}/D_{crit\ p}$ given above would be the same for these two metals, that the slope of the D vs T line and of the rectilinear diameter would be much more gradual than the experimental line The D vs T line for Fe identified by D, if Fe corresponds to Hg, is the uppermost straight line in Fig 1 It is apparent that the disagreement with the observed density line is outside of any

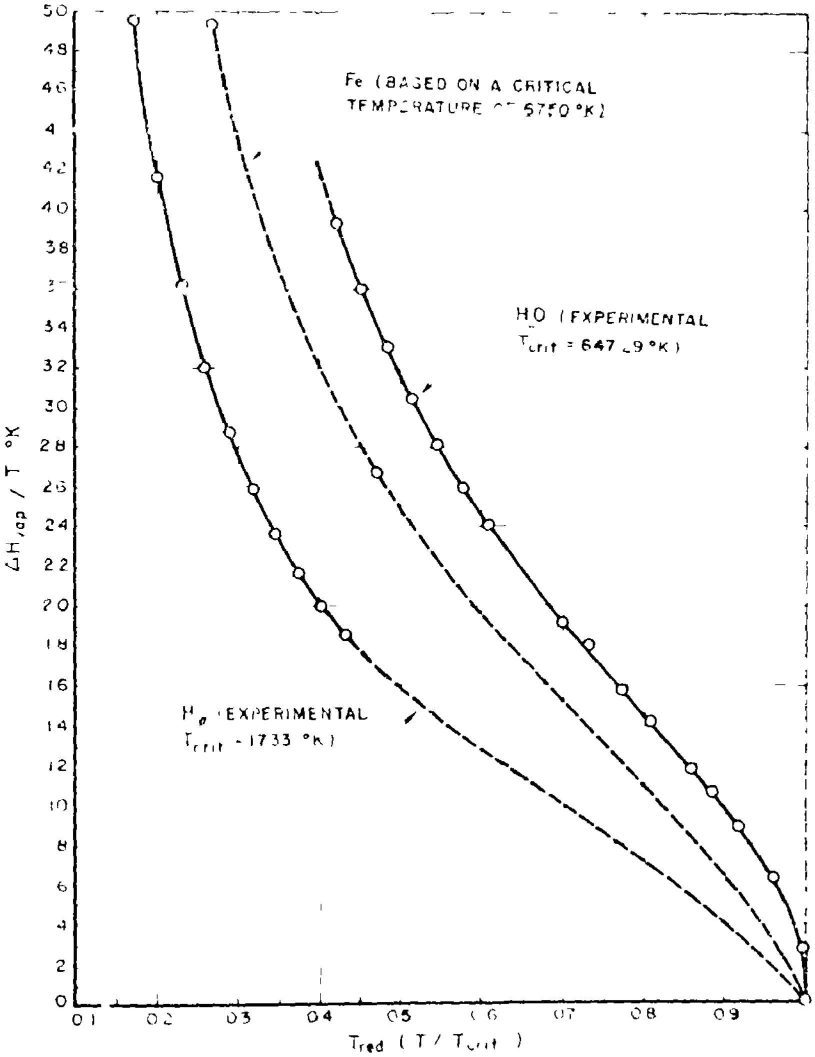


Fig 2

D R Stull and G C Sinke, *Thermodynamic Properties of the Elements* p 112 and 135 Advances in Chemistry Series 18, American Chemical Society, Washington D C (1956) experimental error indicated by the "error cone" of the rectilinear diameter, i.e., D_ϕ, in Fig. 1. The differences in the critical temperatures by the two methods are 3250°K (i.e. 10,000 − 6750 K) for Fe and 4700 K (i.e. 10,700 − 6000°K) for Ni.

If one relies on the experimental liquid densities it follows that the reduced temperatures of Fe and Ni cannot follow the ΔS v. T_{red} curve of mercury. The true ΔS v. T_{red} curve of Fe and Ni estimated from our density measurements, is compared with Hg curve(*) in Fig. 2; a typical homopolar compound, namely H_2O is added as a reference. It is to be expected that some other metals, similar to Fe and Ni, will follow ΔS curves between those of Fe and Ni and the Hg curve.

The reason for this singular behavior of Fe and Ni, and presumably also of Co can be expected to lie in the nature of the metallic bond. Fe, Co and Ni are transition metals with the highest metallic valence of six, in line with PAULING's concepts(12) and the smallest atomic radii (Fe = 1.170 Å, Co = 1.162 Å and Ni = 1.154 Å), these three metals also occupy the minima in the Lothar Meyer atomic volume vs. atomic number curve.

The critical temperature is in a way a measure of the strength of the metallic bond, thus the lower critical temperature than originally expected would imply that the strength of the metallic bond in the Fe-Ni tryad is less than in "simple" metals.

PAULING(13) stresses that "the metallic valence six for iron represents the maximum number of electrons that contribute to the formation of chemical bonds and *not the average* number." He illustrates this point by referring to the equation of state of metals, developed recently by McMILLAN and LATTER(14). These authors showed that an isothermal equation of state can be derived from the coulomb virial theorem for "*simple*" *metals*, consisting of imperturbable metal kernels (ions) embedded in a uniform sea of valence or S electrons. Good agreement could be shown between the ΔH_{form} of the normal gaseous metal ion kernel and the calculated metallic compressibility for the *alkali and alkaline earth metals, where valence shells are entirely constituted of S electrons* (1 and 2 respectively). In the case of transition metals, specifically in the case of Fe, Co and Ni, agreement is reached only if approximately *one half* of PAULING's maximum number of valence electrons was assumed to take part in the metallic bond formation. In the case of *metallic* iron with a valence six and two unpaired electrons occupying separate orbitals, PAULING assumes(13) the configuration $3d^5 4s 4p^2$, in contrast to the *free iron atom*, with a normal ^5D state, based on the configuration $3d^6 4s^2$.

Thus it is probable that in our case also the metallic bond of the typical transition metals, specifically Fe, Co and Ni, is relatively much weaker than in the case of the "simple" metals, i.e. alkali or alkaline earth metals and also Zn, Cd and Hg.

It is likely, therefore, that the other noble metals, i.e. of the VIII group of the periodic system, particularly Pd and Pt, will show lower critical temperatures than previously expected and therefore a much steeper slope in their D vs. T line.

---

* It is based on BUSEY and GIAQUE's measurements(11) of ΔH_{vap} of Hg from its m.p. to 750 K.

(11) R. H. BUSEY and W. F. GIAQUE, *J. Amer. Chem. Soc.* **74**, 801–809 (1953).

(12) L. PAULING, *The Nature of the Chemical Bond* (3rd Ed.), Chap. 11, p. 393–448. Cornell Univ. Press (1960).

(13) L. PAULING, *The Nature of the Chemical Bond*, p. 416. Cornell Univ. Press (1960).

(14) W. G. McMILLAN and A. L. LATTER, *J. Chem. Phys.* **20**, 15 (1958).

J Inorg Nucl Chem 1963 Vol 25 pp 335 to 348 Pergamon Press Ltd Printed in Northern Ireland

PHOSPHORUS-FLUORINE CHEMISTRY—I

FLUORIDES OF PHOSPHONIC AND PHOSPHINIC ACIDS

R Schmutzler
E I du Pont de Nemours & Company, Experimental Station Laboratory
Explosives Department, Wilmington, Delaware

(*Received* 27 *June* 1962)

Abstract —Reaction of methyldichlorophosphine with potassium fluorosulphinate led to the formation of the phosphonic acid fluorides, CH_3POF_2 and CH_3PSF_2, by addition of the elements of sulfur dioxide to the trivalent phosphorus, no fluorophosphine, CH_3PF_2, being observed Dimethylmonochlorophosphine, in the same fashion, was converted into the phosphinic fluorides, $(CH_3)_2POF$ and $(CH_3)_2PSF$ Chloromethyldichlorophosphine, under similar conditions, gave a small amount of the spontaneously inflammable fluorophosphine, $ClCH_2PF_2$, while the principal product corresponded to $ClCH_2PCl_2$ $ClCH_2POF_2$

The synthesis of a number of phosphonic and phosphinic fluorides of the composition $RPOF_2$, $RPSF_2$, R_2POF and R_2PSF (R = aliphatic or aromatic) by metathetical reactions is described Certain phosphonic and phosphinic fluorides were isolated as by-products of the facile partial hydrolysis of the corresponding fluorophosphoranes, RPF_4 and R_2PF_3, respectively

^{19}F nuclear magnetic resonance spectra of substituted aromatic fluorophosphoranes and phosphonic fluorides, whose synthesis is based on dichlorophosphines revealed that aromatic dichlorophosphination under FRIEDEL CRAFTS conditions invariably leads to mixtures of isomers (*p* and *m*) The preparative separation of the tolylphosphonic fluoride isomer mixture by vapour phase chromatography is described

Some infra-red data on phosphonic and phosphinic fluorides are presented

IN 1955 a novel fluorinating agent, potassium fluorosulphinate KSO_2F, was introduced into synthetic chemistry (1a, b) The new reagent permitted the convenient preparation of a variety of fluorine compounds already known as well as providing a route to novel fluorine compounds (cf References 1a d, 2a g)

One of the uses of potassium fluorosulphinate was its application in the fluorination of phosphorus-chlorine bonds, e g for the preparation of phosphorus trifluoride, phosphorus oxyfluoride, phosphorus thiotrifluoride (cf References 1a-b, 3), the phosphonitrilic fluorides (cf References 2a, 2c 2e g), ester derivatives of pentavalent phosphorus,(1d, 3) fluorophosphine complexes of zerovalent nickel(4) and certain fluorides of phosphonic acids (3,4)

In the course of systematic studies on the scope and limitations of fluorinations with potassium fluorosulphinate, its behaviour towards chlorophosphines, $RPCl_2$ and

---

[1a] F Seel, H Jonas, L Riehl and J Langer *Angew Chem* **67**, 32 (1955)

[1b] F Seel and L Riehl, *Z Anorg Chem* **282**, 293 (1955)

[1c] F Seel *Ger Pat* 1000354 (1957)

[1d] F Seel *Ger Pat* 1000355 (1957)

[2a] F Seel and J Langer, *Angew Chem* **68**, 461 (1956)

[2b] F Seel and J Langer, *Z Anorg Chem* **295**, 316 (1958)

[2c] F Seel and J Langer, *Chem Ber* **91**, 2553 (1958)

[2d] F Seel and K Ballreich, *Chem Ber* **92**, 344 (1959)

[2e] A B Burg and A P Caron *J Amer Chem Soc* **81**, 836 (1959)

[2f] A C Chapman, N L Paddock, D H Paine, H T Searle and D R Smith, *J Chem Soc* 3608 (1960)

[2g] A C Chapman, D H Paine, H T Searle D R Smith, and R F M White, *J Chem Soc* 1768 (1961)

[3] F Seel, K Ballreich and R Schmutzler, *Chem Ber* **95**, 199 (1962)

[4] F Seel, K Ballreich and R Schmutzler, *Chem Ber* **94**, 1173 (1961)

R_2PCl was investigated. It was expected that the previously unknown fluorophosphines RPF_2 and R_2PF might be obtained which were deemed to be of interest as novel ligands in co-ordination chemistry.

A vigorous reaction occurred when phenyldichlorophosphine was reacted with potassium fluorosulphinate, both in the presence and absence of a solvent. Instead of being the expected fluorophosphine the product was identified as a constant boiling mixture of the phosphonic fluorides $C_6H_5POF_2$ and $C_6H_5PSF_2$ which could not be separated by distillation. That the product mixture consisted of the phosphonic acid fluorides was demonstrated by the independent synthesis of both compounds.[3,4]

A similar redox reaction was also encountered when methyldichlorophosphine was reacted with potassium fluorosulphinate, the pure phosphonic fluorides CH_3POF_2[5,7a,b,f] and CH_3PSF_2[5,6,7e,k,m] being readily isolable in this case due to a remarkably high difference in boiling points (b.p. CH_3POF_2, 98–99; b.p. CH_3PSF_2, 59–60). Apparently the P—O compound is considerably associated, compared with the P—S derivative, a known property of certain organophosphorus compounds containing P—O and P—S bonds, respectively.[8]

There was no indication for the formation of the fluorophosphine $(CH_3)_2PF$ when dimethylmonochlorophosphine was fluorinated with potassium fluorosulphinate, and the same type of redox reaction as above occurred. The phosphinic fluorides, $(CH_3)_2POF$ and $(CH_3)_2PSF$, were the sole reaction products, identified by vapour phase chromatographic separation of the reaction mixture and comparison with the independently prepared authentic compounds. In a preliminary communication,[11] dimethylmonofluorophosphine was mentioned as a product of the reaction of the chlorophosphine with potassium fluorosulphinate, in the absence of physical or experimental data.

The elements of sulphur dioxide which is generally formed on fluorinations with potassium fluorosulphinate, according to

$$R{-}X + KSO_2F \rightarrow R{-}F + KX + SO_2 \quad (X = \text{halogen})$$

add to the trivalent phosphorus as follows

$$3CH_3PCl_2 + 6KSO_2F \rightarrow 2CH_3POF_2 + CH_3PSF_2 + 6KCl + 5SO_2,$$

$$3(CH_3)_2PCl + 3KSO_2F \rightarrow 2(CH_3)_2POF + (CH_3)_2PSF + 3KCl + 2SO_2$$

---

[5] T. P. DAWSON and K. C. KENNARD, *J. Org. Chem.* **22**, 1671 (1957).

[6] G. SCHRADER (to Farbenfabriken Bayer A. G.), *Ger. Pat.* 1099532 (1961).

[7][a] H. COATES and P. R. CARTER (to Great Britain Ministry of Supply), *Brit. Pat.* 734187 (1955), *U.S. Pat.* 2853515 (1958).

[b] A. I. RAZUMOV, O. A. MUKHACHEVA and E. A. MARKOVICH, *J. Gen. Chem. USSR* (Eng. Transl.) **28**, 194 (1958).

[c] M. HALMANN, *J. Chem. Soc.* 305 (1959).

[d] L. M. YAGUPOL'SKII and ZH. M. IVANOVA, *J. Gen. Chem. USSR* (Eng. Transl.) **29**, 3726 (1959).

[e] G. SCHRADER (to Farbenfabriken Bayer A. G.), *Belg. Pat.* 588254 (1960).

[f] P. J. R. BRYANT, A. H. FORD-MOORE, B. J. PERRY, A. W. H. WARDROP and T. F. WATKINS, *J. Chem. Soc.* 1553 (1960).

[g] G. SCHRADER (to Farbenfabriken Bayer A. G.), *Ger. Pat.* 1085874 (1960).

[h] C. W. TULLOCK and D. D. COFFMAN, *J. Org. Chem.* **25**, 2016 (1960).

[i] L. M. YAGUPOL'SKII and ZH. M. IVANOVA, *J. Gen. Chem. USSR* (Eng. Transl.) **30**, 3986 (1960).

[k] G. SCHRADER (to Farbenfabriken Bayer A. G.), *French Pat.* 1250923 (1960).

[l] V. GUTMANN, P. HEILMAYER and K. UTVARY, *Monatsh. Chem.* **92**, 196 (1961).

[m] I. P. KOMKOV, S. Z. IVIN, K. W. KARAVANOV, and L. JE. SMIRNOV, *Zh. Obshchei Khim.* **32**, 301 (1962).

[8] G. M. KOSOLAPOFF, *Organophosphorus Compounds*, p. 241 ff. J. Wiley, New York and London (1950).

A particularly interesting observation was made in the reaction of chloromethyldichlorophosphine, $ClCH_2PCl_2$, with potassium fluorosulphinate With antimony trifluoride, chloromethyldichlorophosphine was converted smoothly into the spontaneously flammable fluorophosphine, $ClCH_2PF_2$ (10) while a variety of other chlorophosphines were invariably converted to fluorophosphoranes, R_nPF_{5-n} (cf below) With potassium fluorosulphinate as a fluorinating agent, small amounts of the fluorophosphine, $ClCH_2PF_2$, and of the phosphonothioic difluoride, $ClCH_2PSF_2$ were formed, while the bulk of the product, b p 119°, had the composition

$$ClCH_2PCl_2\ ClCH_2POF_2$$

(cf b p $ClCH_2PCl_2$ 129°, b p $ClCH_2POF_2$ ~ 128°) The same 1 1 product was obtained on combination of equimolar amounts of the pure components, no noticeable heat of reaction being observed The refractive index of the 1 1 product was found to be almost linearly related to the indices of the pure components, suggesting a relatively weak molecular interaction

A comparison of the ^{19}F nuclear magnetic resonance spectrum (at 56 4 mc/s) of pure chloromethylphosphonic difluoride and of its 1 1 product with chloromethyldichlorophosphine showed a doublet, P - F coupling constant J 1140 c/s, at the same position in both products, again favouring the formulation of the 1 1 product as a mere azeotrope

The infra-red spectrum appeared essentially as superimposed from the pure components, except for the P O absorption in chloromethylphosphonic difluoride, which was raised by ca 20 cm^{-1} The product may be regarded as an azeotrope, especially in view of its boiling point being slightly lower than the boiling points of the individual pure components On the gas chromatography column the product was readily separated into its components, and no peaks besides pure chloromethyldichlorophosphine and chloromethylphosphonic difluoride were detected The exact 1 1 composition of the product, however, is noteworthy A study on the interaction between chloromethylphosphonic difluoride and certain other trivalent phosphorus compounds in view of the above observations may be of interest

Further attempts to prepare fluorophosphines by conventional fluorination methods either failed or led to similar redox reactions It must be concluded, therefore, that fluorophosphines are strongly reducing compounds and in fact the first representatives of this new class of compounds(9, 10) were found to be highly reactive, flammable materials Fluorophosphines co-ordinated to a zerovalent transition metal e g nickel, could readily be obtained by fluorination of nickel-chlorophosphine complexes with potassium fluorosulphinate(4) The fluorination of chlorophosphines R_nPCl_{3-n} with Group V fluorides usually led to fluorophosphoranes R_nPF_{5-n} in excellent yield, instead of the expected derivatives of trivalent phosphorus R_nPF_{3-n}, where n 1 or 2(7, 10)

An extensive study of organophosphorus fluorine compounds(10) led to the preparation of a number of phosphonic and phosphinic acid fluorides, $RP(X)F_2$ and $R_2P(X)F$ (R organic group, X O S) whose synthesis and properties are discussed below Phosphonic and phosphinic fluorides represent a new class of compounds, and a few

---

(9) N Kulakova, Yu M Zinov'ev and L Z Soborovskii *J Gen Chem USSR* (Eng Transl) 29 3916 (1959)

(10) Schmutzler *Chem and Ind* 1868 (1962) and subsequent publications

representative examples have been described only recently, almost simultaneously by several different workers.(5, 6, 7, 10) Usually the synthesis was by fluorination of the corresponding chlorides with hydrogen fluoride, alkali fluorides in polar solvents like tetramethylene sulphone or acetonitrile, potassium fluorosulphinate, potassium bifluoride, zinc fluoride, benzoyl fluoride, sodium hexafluorosilicate, etc.

In the present work, some of the above mentioned fluorinating agents were also employed. In addition, advantage was taken from the strongly reducing properties of fluorophosphines, which permitted a simple synthesis of phosphonic fluorides: dichlorophosphines were reacted with alkali fluorides in a polar solvent like acetonitrile in the presence of air and a catalyst, e.g.

$$C_6H_5PCl_2 + \tfrac{1}{2}O_2 + 2NaF \xrightarrow[(SbCl_5)]{Sb_2O_3} C_6H_5POF_2 + 2NaCl$$

The combination of antimony trifluoride with catalytic amounts of antimony pentachloride was used in a few instances (e.g. chloromethyl groups bonded to phosphorus in phosphonic chlorides). No attack on the carbon–chlorine bond was noted while the *phosphorus chlorine bond was readily fluorinated*.

Phosphonic and phosphinic fluorides were frequently obtained on the preparation of the corresponding fluorophosphoranes, RPF_4 and R_2PF_3,(10) particularly if moisture was not rigorously excluded. Due to the marked difference in reactivity of fluorine atoms in RPF_4 (and R_2PF_3) compounds, it was also possible to effect their partial hydrolysis under controlled conditions (temperature below 0°) with an equimolar amount of water, preferably in a solvent, e.g.

$$RPF_4 + H_2O \xrightarrow{0°} RPOF_2 + 2HF \rightarrow (\xrightarrow{\text{excess } H_2O} RPO(OH)_2)$$

It was also found in certain instances that on prolonged storage in glass fluorophosphoranes were converted to the corresponding phosphonic fluorides, e.g.

$$C_2H_5PF_4 \rightarrow C_2H_5POF_2$$

Phosphonic and phosphinic acid fluorides are relatively easy to handle, as compared with the corresponding fluorophosphoranes, the latter being far more sensitive towards hydrolysis. Compounds of the type $RPSF_2$ are more stable towards hydrolysis than $RPOF_2$ compounds, while $R_2P(X)F$ compounds ($X = O$ or S) are generally more stable than $RP(X)F_2$. Some of the compounds possessed an unpleasant odour which may be partially due to small amounts of impurities since highly purified compounds, particularly $RPOF_2$ and R_2POF, were found to be almost odourless. Characteristic is the smell of certain compounds containing the $-PSF_2$ group, some of them also fuming slightly in the atmosphere. Preliminary screening on possible biological properties of phosphonothioic difluorides revealed activity of a lower order as compared with phosphinothioic monofluorides, R_2PSF(7g) or phosphonamidothioic difluorides, $RP(S)(NR_2)F$(6, 7e, k) the latter being readily obtained upon interaction of secondary amines with phosphonothioic difluorides. These novel types of compounds are distinguished by their high insecticidal activity. Useful insecticides of the composition $R\,C_6H_4P(X)(OR')F$ ($X = O$ or S) have been obtained via the phosphonic difluorides.(11a) An independent synthesis of the same type of compounds has been described simultaneously.(11b)

---

(11)a G. SCHRADER (to Farbenfabriken Bayer A.G.), *Ger. Pat.* 1071702 (1959).

b L. M. YAGUPOL'SKII and ZH. M. IVANOVA, *J. Gen. Chem. USSR* (Eng. Transl.) **30**, 1310 (1960).

Except for the above mentioned examples, little is known about the chemistry of phosphonic or phosphinic fluorides It has been demonstrated that $RPOF_2$ intermediates are useful in the synthesis of unsymmetrical phosphinic acids via the GRIGNARD reaction (5) In a similar manner, phosphonic fluorides were employed as convenient intermediates in the synthesis of tertiary phosphine oxides, which are of current interest with respect to their application as high-temperature stable fluids (12) The electronegativity of the fluorine apparently facilitated the nucleophilic attack on the phosphorus atom in the Grignard reaction, where the corresponding chloro compounds failed to react in a defined manner Phenylphosphonic difluoride was the starting material for an interesting synthesis of the tetrafluorophosphorane, $C_6H_5PF_4$ by fluorination of the P O group with sulphur tetrafluoride (13)

In connection with the present work, some interesting information was obtained on the orientation of phosphorus in the extensively explored and widely applied process of aromatic dichlorophosphination

A standard method for the preparation of aromatic dichlorophosphines consists in the reaction of aromatic hydrocarbons with phosphorus trichloride/aluminium chloride, i e under Friedel-Crafts conditions, first introduced by MICHAELIS almost seventy years ago (14a,b)

$$R\,C_6H_5 \quad PCl_3 \xrightarrow{AlCl_3} R\,C_6H_4\,PCl_2 \quad HCl$$

Although MICHAELIS considered the possibility of isomers in this reaction, little attention has been given to this question, since, and until recently the procedure was described to give essentially the para-isomers (cf 15–21, for example)

KOSOLAPOFF (18) assumed the presence of *ortho* and *para*-isomers in a phosphonate synthesis based on the corresponding aromatic dichlorophosphine and reported later the formation of *o*, *m*, and *p*-isomer in the dichlorophosphination of toluene (22) Some criticism of the classical Friedel-Crafts method has also been offered by ERLENMEYER (23,24), who reported for the first time an unambiguous synthesis of *o*- and *p*-tolyldichlorophosphine It is obvious that boiling points and refractive indices of the isomeric compounds show only little difference, and usually the reaction products of the Friedel-Crafts synthesis were regarded and used as *p*-substituted dichlorophosphines

Recent work of MUETTERTIES (25a,b), however, showed that dichloroborination of aromatic hydrocarbons under similar conditions as the dichlorophosphination invariably led to mixtures of *m*- and *p*-isomers (a *m*:*p*-ratio between 1:1.5 and 1:5 being observed) whereas the *o*-isomer seems to be less favoured from sterical reasons. The isomer ratio was readily established by perhydrolysis of the dichloroborane mixture with subsequent IR identification of the corresponding substituted phenols.

---

(12) D GRAFSTEIN, R DUDAK and M S COHEN WADC Technical Report 57-45, Part III

(13) W C SMITH, *J Amer Chem Soc* **82**, 6176 (1960)

(14a) A MICHAELIS, *Ann* **293**, 193 (1896)

(b) A MICHAELIS *Ann* **294**, 1 (1896)

(15) J K JACKSON, W C DAVIES and W J JONES, *J Chem Soc* 2298 (1930)

(16) W C DAVIES and W P WALTERS, *J Chem Soc* 1786 (1935)

(17) W J JONES, W C DAVIES, S T BOWDEN, C EDWARDS, V C DAVIS and L H THOMAS *J Chem Soc* 1446 (1947)

(18) G M KOSOLAPOFF and W F HUBER, *J Amer Chem Soc* **69**, 2020 (1947)

(19) Z I KHISAMOVA and G KAMAI, *J Gen Chem USSR* (Eng Transl) **20**, 1207 (1950)

(20) B BUCHNER and L G LOCKHART, *J Amer Chem Soc* **73**, 755 (1951)

(21) R H WILEY and C H JARBOE, *J Amer Chem Soc* **73**, 4496 (1951)

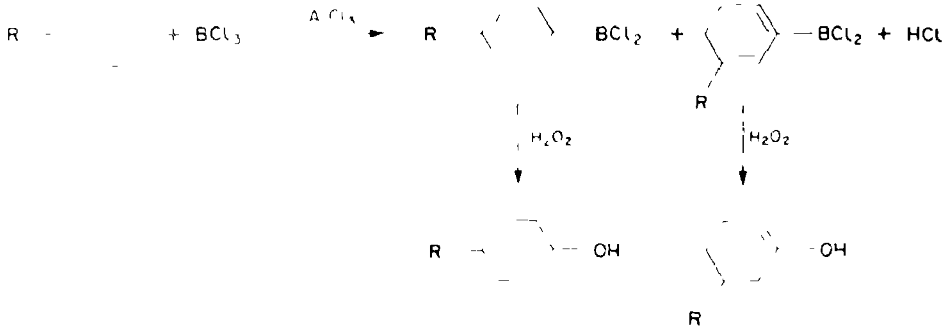
(22) G M KOSOLAPOFF *J Amer Chem Soc* **74**, 4119 (1952)

(23) TH WEIL, B PRIJS and H ERLENMEYER, *Helv Chim Acta* **35**, 1412 (1952)

(24) TH WEIL, B PRIJS and H ERLENMEYER, *Helv Chim Acta* **36**, 1314 (1953)

(25a) E L MUETTERTIES, *J Amer Chem Soc* **81**, 2597 (1959)

(b) E L MUETTERTIES, *J Amer Chem Soc* **82**, 4163 (1960)



A similar approach for dichlorophosphines is difficult due to the great stability of the carbon phosphorus bond.

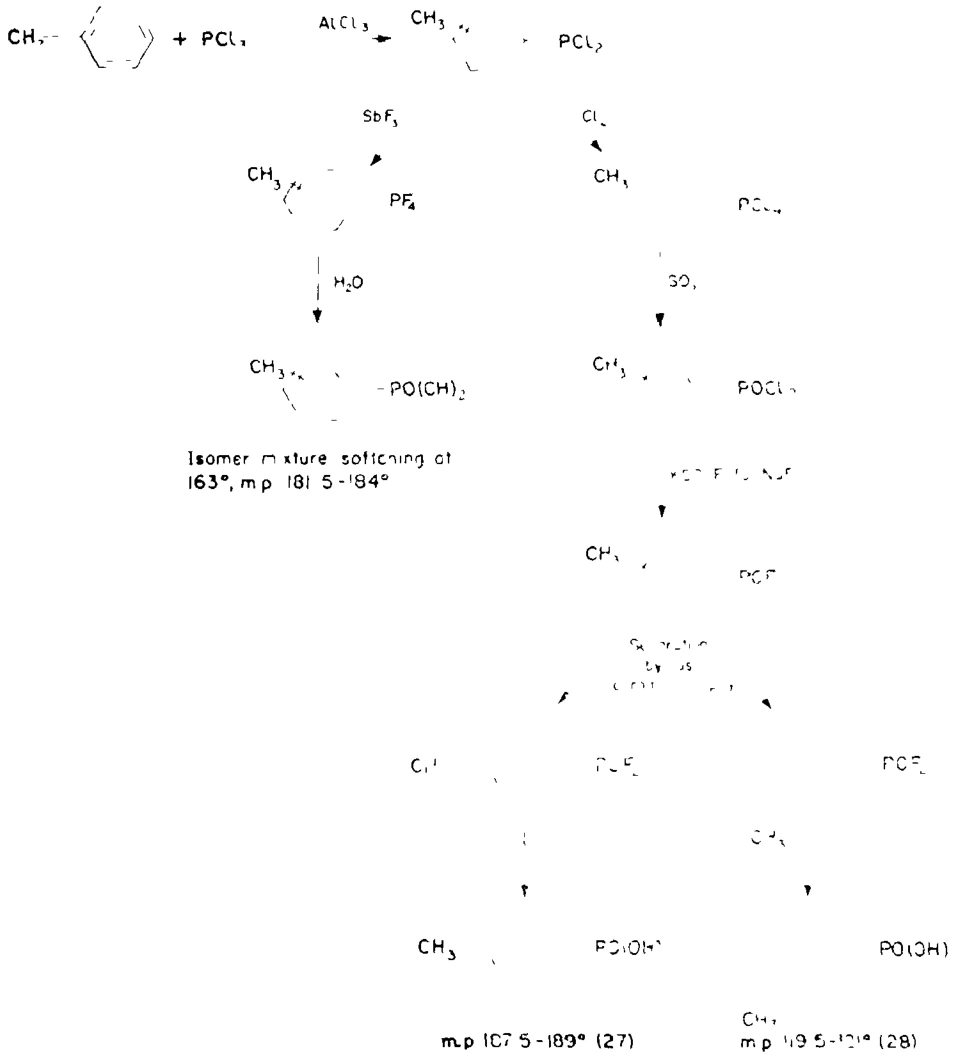
Fluorine (^{19}F) nuclear magnetic resonance spectra of several substituted aromatic fluorophosphoranes were taken of tolyl-, chlorophenyl-, methoxyphenyl- and isopropylphenyl-tetrafluorophosphorane(20) whose synthesis(10) is based on the corresponding dichlorophosphines. In every case the presence of at least two different species, presumably aromatic isomers, was revealed. The ^{19}F nuclear magnetic resonance spectrum of the aryl-tetrafluorophosphoranes was found to consist of a single resonance split into a doublet by ^{31}P, these data being consistent with a tetragonal pyramid structure with the aryl group at the apical position. The data can also be interpreted, however, in terms of a trigonal bipyramidal structure, and an intramolecular exchange process may be responsible for the NMR-spectroscopical equivalence of the fluorine atoms in fluorophosphoranes.

For the isomer mixture of the tolyl tetrafluorophosphoranes a P–F coupling constant of 960 c/s and an isomer ratio of ca. 2:1 was found. The corresponding data for tolylphosphonic difluoride which was prepared from the same tolyldichlorophosphine, are 1099 c/s and ca. 2:1, respectively. Similarly, on gas chromatography analysis of the tolyltetrafluorophosphorane two peaks in an approximate ratio between 2:1 and 3:1 were observed. A preparative separation by gas chromatography in order to establish the identity of the isomers was then carried out on the tolylphosphonic difluorides since the highly reactive tetrafluorophosphoranes presented some handling difficulties. The reliability of the gas chromatography method was checked by running authentic samples of phenyltetrafluorophosphorane (1 peak), phenylphosphonic difluoride (1 peak), and isopropyl phenyltetrafluorophosphorane (2 components). It was impossible to analyse the original tolyldichlorophosphine under a variety of conditions without sizeable decomposition. It can, however, be safely assumed that the isomer distribution found in tolyltetrafluorophosphorane and

(20) E. L. MUETTERTIES, R. SCHMUTZLER and W. MAHLER. Submitted for publication.

tolylphosphonic difluoride also represents the composition of the starting tolyldichlorophosphine Both analytical and preparative gas chromatography on the tolylphosphonic difluoride mixture showed an isomer ratio close to 2:1 (*p*:*m*, as will be demonstrated below). One of the separated isomers (*p*) was found to be solid at room temperature, while the other pure component was liquid Both separated products were hydrolysed to give the corresponding phosphonic acids which were shown to be identical with authentic products, as summarized below Hydrolysis of the original tolyltetrafluorophosphorane gave a mixture of isomeric phosphonic acids melting over a range

Dichlorophosphination of Toluene



The results described do not rigorously exclude the presence of *ortho* compound but strongly support the presence of only two isomers in tolyldichlorophosphine, as obtained by the Friedel-Crafts method. A comparison of the refractive indices of pure *o*- and *p*-tolyldichlorophosphine(23, 21) with the value for the isomer mixture again indicates that the impurity of the *p*-isomer is *m* rather than *o*.

---

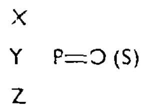
(27) A BURGER and N D DAWSON *J Org Chem* 16, 1250 (1951) reported m p 188 5 190

(28) J M DENHAM and R K INGHAM *J Org Chem* 23, 1298 (1958) reported m p 125 126 , a mixed m p with an authentic sample kindly provided by Prof R K Ingham was undepressed (softening from 121°), and the acids were found to be identical by their infra-red spectra

BALDWIN *et al.*(29) recently reported similar observations on the formation of isomers in the aromatic dichlorophosphination using a different approach to establish the isomer ratio. Ethylphenyldichlorophosphine, for instance, was found to contain *p*- and *m*-isomer in a ratio 1.63 : 1, similar to tolyldichlorophosphine, as described above.

Infrared spectra of phosphonic and phosphinic fluorides

No observations on the infra-red spectra of phosphonic or phosphinic fluorides have been reported so far. In the course of the present work some data on the spectra of



$$\begin{matrix} X & \\ Y & P{=}O\,(S) \\ Z & \end{matrix}$$

compounds, where X and Y may represent F and Z = an organic group, or X = F and Y and Z = organic groups, were obtained and are summarized in Tables 1–4. For P=O compounds an empirical relation between the electronegativity of the substituents in XYZP=O and the position of the P=O stretching frequency was given by BELL *et al.*(30)

$$\lambda(\mu) = \frac{39.96 - \Sigma x}{3.995} \qquad \text{(A)}$$

where $\lambda(\mu)$ = phosphoryl absorption wavelength

Σx = sum of the phosphoryl absorption shift constants, derived from Pauling electronegativities.

Supported by data obtained on numerous different types of XYZP=O molecules with various substituents X, Y and Z, it was concluded that the effects of substituents upon the position of the P=O stretching frequency are constant and additive. It was therefore deduced that for this correlation the band-shifts observed are determined mainly by the electrical effect of the substituents upon the force constant rather than by mass effects. The results now obtained on numerous compounds of the types $RPOF_2$ and R_2POF (R = organic group) are in good agreement in most instances with the values calculated using Equation (A) and the phosphoryl absorption shift constants, as given by BELL *et al.*(30) Where available, data on the corresponding chloro compounds, $RPOCl_2$ and R_2POCl, are also included. The shift of the P=O absorption towards higher wave numbers, according to an increased double bond character, on substitution of chlorine by the more electronegative fluorine is obvious. P—F stretching frequencies also included in the table are derived from a comparison of $RPOF_2$ and R_2POF compounds with either the corresponding chloro compounds $RPOCl_2$ and R_2POCl, or with the chlorophosphines, $RPCl_2$ and R_2PCl, respectively.

---

(29) R. A. BALDWIN, K. A. SMITHEMAN and R. A. WASHBURN, *J. Org. Chem.* **26**, 3547 (1961).

(30) J. V. BELL, J. HEISLER, H. TANNENBAUM and J. GOLDENSON, *J. Amer. Chem. Soc.* **76**, 5185 (1954).

of the P S absorption was found to be very variable, and some P S compounds did not show any absorption to be assigned to P S HOOGE and CHRISTEN(33) reported some semiquantitative considerations on the infra-red spectra of P S compounds In view of the small differences of electronegativities between P and S, implying only a small amount of ionic character of the P S bond as compared with P O, electronegative substituents may be expected to have only little influence on the position of the P S stretching frequency The assignments for P S stretching frequencies made in the present work were obtained by comparison of the spectra of P =S compounds with the corresponding sulphur-free compounds but most of the data are only tentative and quite uncertain

TABLE 5a —P S AND P F INFRA-RED ABSORPTIONS IN $RPSF_2$ AND R_2PSF COMPOUNDS

Compound	νP S (cm^{-1}) found	νP F (cm^{-1})
CH_3PSF_2	?	856 vs 845 vs
$ClCH_2PSF_2$	659 vs (?)	916 vs 888 vs
$C_2H_5PSF_2$	?	ca 870 vs (bd)
i-$C_5H_{11}PSF_2$	ca 680 vs (?)	882 vs 856 vs
C_6H_5CH $CHPSF_2$	?	905 vs 873 vs
$C_6H_5PSF_2$	?	895 vs 870 vs
$(CH_3)_2PSF$	756 vs	794 s (?)
$(C_6H_5)_2PSF$	738 vs (?)	827 vs

TABLE 5b P S INFRA-RED ABSORPTION IN $RPSCl_2$ AND R_2PSCl COMPOUNDS

Compound	νP S (cm^{-1})	Lit reference
CH_3PSCl_2	664*	36
$C_2H_5PSCl_2$	Triplet at 680, 665, 640	36
i-$C_5H_{11}PSCl_2$	ca 680 vs bd (?)	
$C_6H_5PSCl_2$	745 s	37
$(C_6H_5)_2PSCl$	735 vs (?)†	

* Comparison of the infra-red spectra of CH_3PCl_2 and CH_3PSCl_2 shows clearly one strong new band at 780 cm^{-1} in the latter Assignment to the P – S stretch however, is doubtful,(33 36) and assuming νP – S at 665 cm^{-1} seems to be more justified

† $(C_6H_5)_2PCl$ absorbs at 745 cm^{-1} but the intensity of the 735 cm^{-1} band in $(C_6H_5)_2PSCl$ is greatly increased as compared with $(C_6H_5)_2PCl$, possibly due to the new P S absorption

EXPERIMENTAL

A *Reaction of chlorophosphines with potassium fluorosulphinate*

The reaction of phenyldichlorophosphine with potassium fluorosulphinate has been described in a previous paper (4)

Interaction of methyldichlorophosphine with potassium fluorosulphinate One hundred and twenty grammes of Technical grade (ca 35 per cent) potassium fluorosulphinate (Ozark Mahoning Co) was suspended in 100 ml abs decalin under nitrogen An exothermic reaction started immediately

---

(34) H S GUTOWSKY and A D LIEHR, *J Chem Phys* **20**, 1652 (1952)

(35) J QUINCHON, M LESECH and E GRYSZKIEWICZ-TROCHIMOWSKI, *Bull Soc Chim France* 169 (1962)

(36) E M POPOV, T A MASTRYUKOVA, N P RODIONOVA, and M I KABACHNIK, *J Gen Chem USSR* (Eng Transl) **29**, 1967 (1959)

(37) L W DAASCH and D C SMITH, U S Naval Research Laboratory Report No 3657 (1950).

on the dropwise addition of 35 g (0 3 mole) methyldichlorophosphine, and reflux of a low boiling material was observed When the addition of the chlorophosphine was completed (50 min) the mixture was heated for 2 hr at 70 inner temperature Distillation at atmospheric pressure gave 27 9 g (88 2 per cent) of CH_3PSF_2/CH_3POF_2, b p 57–99

On redistillation (10 in helix-packed column) 4 9 g CH_3PSF_2 (b p 59–60 * after fractionation, in agreement with Reference 3), and 13 2 g CH_3POF_2, b p 98 99 , n_D^{25} 1 3170, was obtained †

Reaction of dimethylmonodichlorophosphine with potassium fluorosulphinate This reaction was studied in essentially the same way as described above for methyldichlorophosphine The starting chlorophosphine was prepared according to the directions of PARSHALL(38) with the modification that the crude mixture of dimethylchlorophosphine-dimethylphosphinothioic chloride was redistilled, over tributylphosphine The yield of dimethylchlorophosphine could thus readily be doubled

Dimethylchlorophosphine 19 3 g (0 2 mole), was distilled into a dropping funnel attached to a 200 ml three-necked flask fitted with a reflux condenser and a mechanical stirrer in which 50 g technical potassium fluorosulphinate had been suspended in 100 ml benzene under strict exclusion of air and moisture A strongly exothermic reaction occurred on the dropwise addition of the chlorophosphine to the stirred suspension After the addition was completed the mixture was refluxed for 5 hr The cooled mixture was filtered under nitrogen at atmospheric pressure and the volatile products were distilled off over a Vigreux column Boiling point and refractive index of the distillate confirmed its identity as virtually pure benzene A compound $(CH_3)_2PF$ would be expected to have a boiling point of approximately 40–50 (b p $(CH_3)_2PCl$ 75) Several samples of the distillate were also analysed by gas chromatography,‡ and found to contain only negligible impurities, which did not show up in the infra-red spectrum

The higher boiling residue was then distilled in a vacuum over a 4 in Vigreux column to give a total of 12 5 g 61 5 per cent of a colourless liquid, b p 60–72 20 mm Two cuts, having the following refractive indices were taken

$$(1)\ n_D^{21\ 2}\quad 1\ 4590 \qquad (2)\ n_D^{3\ 4}\quad 1\ 4216$$

By comparison with the refractive indices of the pure components ($(CH_3)_2POF$ $n_D^{3\ 8}$ 1 3940, $(CH_3)_2PSF$ $n_D^{3\ 8}$ 1 4875) the molar ratio $(CH_3)_2POF$ $(CH_3)_2PSF$ was found to be ca 7 3 in the first cut and ca 3 7 in the second This result is in good agreement with the ratio derived from the VPC data obtained for cut 2 at 77 (40 cm³ min , 20 per cent silicon grease on 60 80 super support) I peak at 4 7 min $(CH_3)_2POF$ I peak at 5 3 min $(CH_3)_2PSF$, approximate ratio ca 3 7 No by-products were detected by VPC Identification of the components was by comparison with authentic $(CH_3)_2POF$ and $(CH_3)_2PSF$ The change in composition of cut (1) and (2) is also reflected in the infra-red spectra the P O stretching frequency at 1250 cm $^{-1}$ is much stronger in cut (1) than in cut (2), in accordance with the decreasing $(CH_3)_2POF$ content in the latter

Reaction of chloromethyldichlorophosphine with potassium fluorosulphinate There was no immediate exothermic reaction when 45 5 g (0 3 mole) chloromethyldichlorophosphine (39) was added dropwise to a suspension of 110 g technical potassium fluorosulphinate in 130 ml *o*-dichlorobenzene under nitrogen Slight reflux of a lower boiling product was noted when the mixture was stirred at gradually increasing temperature up to 110 (2 hr) Distillation at atmospheric pressure gave first 5 5 g of a spontaneously flammable liquid b p 33 40 ($ClCH_2PF_2$ c f 10) Only 0 3 g of $ClCH_2PSF_2$ b p 87–94 , n_D^{25} 1 4430 (identified by b p and refractive index) was then isolated The higher boiling products were recovered under vacuum (ca 50 mm) and redistilled at atmospheric pressure and 15 6 g of a colourless liquid, b p 119 120 was collected On redistillation the b p was unchanged at 119 , n_D^{26} 1 4520 (cf $ClCH_2POF_2$ n_D^{20} 1 3720, $ClCH_2PCl_2$ n_D^{25} 1 52 82) Found C, 8 4 H 1 6, P, 21 8, F, 13 4 Calc for $ClCH_2PCl_2$ $ClCH_2POF_2$(285 8) C 8 4 H 1 4 P 21 7, F, 13 3 %)

Direct combination of chloromethyl dichlorophosphine with chloromethylphosphonic difluoride No exothermic reaction occurred when 11 5 g (0 076 mole) chloromethyldichlorophosphine was added dropwise to 10 0 g (0 076 mole) chloromethylphosphonic difluoride Distillation of the mixture at atmospheric pressure (under nitrogen protection) gave 21 0 g (97 per cent) of a colourless liquid, b p 119–120 , $n_D^{26\ 5}$ 1 4470 Boiling point and refractive index remained unchanged on redistillation over a 10 in helix-packed column Physical data and analysis confirmed that the product was the same as above. Found: C, 8.6, H, 1.8, P, 22.0, F, 13.7, Cl, 49.1. Calc for $ClCH_2PCl_2 \cdot ClCH_2POF_2$ (285.8): C, 8.4, H, 1.4, P, 21.7, F, 13.3, Cl, 49.6%.)

---

* The b p 84° for CH_3PSF_2, as reported by SCHRADER(6, 7c, k) must be corrected (G SCHRADER, personal communication), a difference of only 14 (84 vs 98) between the b p of CH_3PSF_2 and $C_2H_5PSF_2$ would be unlikely In the meantime in another paper(7m) a b p of 61 62 was reported

† DAWSON and KENNARD(5) reported for CH_3POF_2 b p 98 99 , n_D^{25} 1 3148 while RAZUMOV and coworkers (7b) presumably had an impure product, reporting n_D^{20} 1 3277

‡ The author is indebted to Mr C R TALLEY for the gas chromatography work described herein

(38) G W PARSHALL, *J Inorg Nucl Chem* **12**, 372 (1960)

(39) F UHING, K RATTENBURY and A D F TOY, *J Amer Chem Soc* **83**, 2299 (1961)

Infra-red spectra. The infra-red spectra were recorded on the pure components chloromethyldichlorophosphine and chloromethylphosphonic difluoride and on the 1:1 products obtained upon interaction of $ClCH_2PCl_2$ with KSO_2F (A) and on direct combination of $ClCH_2PCl_2$ with $ClCH_2POF_2$ (B) respectively.

The spectra of the 1:1 products appear essentially as a superposition of the spectra of the pure components except for a strong absorption in product A at 1719 cm^{-1}, which cannot be explained, but may be due to an unknown impurity. The considerable shift of the P–O stretching frequency (1332 vs. 1352 cm^{-1}) indicates that this bond is involved in the interaction with the chlorophosphine while most of the other absorptions are virtually unchanged.

Gas chromatography on $ClCH_2PCl_2 \cdot ClCH_2POF_2$. $ClCH_2PCl_2 \cdot ClCH_2POF_2$ was clearly separated into two pure components (104°, 60 cm^3 carrier gas/min, 6 ft silicon oil column, 20 per cent on 60-80 super support), retention times 2.2 and 6.3 min, respectively. Comparison with authentic samples showed the 2.2 min peak to be chloromethylphosphonic difluoride while the 6.3 min peak was due to chloromethyldichlorophosphine.

$ClCH_2PCl_2$	$ClCH_2POF_2$	$ClCH_2PCl_2 \cdot ClCH_2POF_2$ (A)	$ClCH_2PCl_2 \cdot ClCH_2POF_2$ (B)	
2980 m	2990 m	2990 s	2990 s	νC–H
		2930 s	2930 s	
		1719 vs		
1388 vs	1395 m	1388 s	1388 s	δC–H
	1332 vs	1352 vs	1352 vs	νP–O
1286 vs		1276 m*	1280 vw	
	1232 m	1230 s	1229 s	
		1188 m	1187 m	
	1138 w	1134 m	1132 m	
	930 vs	930 vs	930 vs	νP–F
	916 vs	917 vs	917 vs	
	899 s	901 s	901 s	
810 vs		813 s	813 s	
	795 m	796 s	796 s	
775 m		775 w	775 w	
746 s		746 s	746 s	
	712 sh	713 s	713 s	
	704 s	704 s	704 s	νC–Cl
682 vs		683 s	683 s	

* Position of band shifts with dilution with a solvent, e.g. benzene.

B. *Reaction of phenyldichlorophosphine with sodium fluoride/oxygen in acetonitrile in the presence of a catalyst*

Only trace amounts of phenylphosphonic difluoride were detected when air was bubbled through the stirred suspension of sodium fluoride in acetonitrile phenyldichlorophosphine for 16 hr at 80°, and most of the dichlorophosphine was recovered unchanged. The reaction was more efficient when antimony trioxide or antimony pentachloride was added as a catalyst.

In a typical experiment, 63 g (1.5 mole) sodium fluoride + 1 g antimony trioxide was suspended in a mixture of 89.5 g (0.5 mole) phenyldichlorophosphine and 130 ml acetonitrile, and air was bubbled through the suspension with stirring at reflux for 10 hr. After removal of the solids by filtration, 55 g of distillate, b.p. 40-84°/19 mm, n_D^{25} 1.4740 was obtained, no unreacted $C_6H_5PCl_2$ was found. On redistillation, 20 g of a product, b.p. 37-40°/18 mm (129-130°/760 mm), n_D^{25} 1.4812 was isolated, but not identified, while 22 g of the desired pure phenylphosphonic difluoride, b.p. 77°/15 mm, n_D^{25} 1.4645 was further obtained. Identification of phenylphosphonic difluoride was by boiling point, refractive index and infra-red spectrum.[1] In another run, the amount of the lower boiling by-product was substantially lower. Antimony pentachloride was found to have catalytic properties similar to antimony trioxide.

C. *The fluorination of phosphonic or phosphinic chlorides with potassium fluorosulphinate*

The fluorination was conducted by suspending excess potassium fluorosulphinate (technical product of Ozark Mahoning Co.) in benzene, and dropwise addition of the compound to be fluorinated to the stirred suspension, the reaction being exothermic in some cases. The reaction mixtures were stirred until the evolution of sulphur dioxide had ceased (2–10 hr), and the products were isolated by vacuum distillation after removal of the solids by filtration and distillation of the solvent

D *Fluorination with antimony trifluoride*

These reactions were carried out in a three-necked flask fitted with a reflux condenser, thermometer, and a solid addition funnel, the latter containing a slight excess of antimony trifluoride The P–Cl compound, together with a few drops of antimony pentachloride was placed into the flask under nitrogen An exothermic reaction occurred when the antimony trifluoride was gradually added, a temperature of ca 50–60 being maintained Stirring at this temperature was continued for 1–2 hr and the product was isolated by distillation

In the specific examples investigated the addition of antimony pentachloride could probably have been omitted since a fluorination of the C–Cl bond did not occur, and P–Cl compounds normally react with antimony trifluoride in the absence of a catalyst

E *Benzoylfluoride as a fluorinating agent*

This compound(7h) was used in slight excess in combination with small amounts of antimony pentachloride as a catalyst The P–Cl compound was added to the benzoyl fluoride with stirring and a temperature of 100–150° was maintained for ca 3 hr The fluorination products were isolated by distillation

F *Fluorinations with sodium fluoride in tetramethylene sulphone* (*TMSO*)

These reactions were carried out according to the directions of TULLOCK and COFFMAN(7h) by the dropwise addition of the P–Cl compound to excess oven-dried sodium fluoride, suspended in TMSO, with stirring The reaction mixtures were stirred at elevated temperature for the period indicated, and the fluorides were isolated by distillation, followed by careful fractionation

G *Controlled hydrolysis of fluorophosphoranes*

A typical example is as follows chlorophenyltetrafluorophosphorane(7d, 10) was dissolved in a small amount of tetrahydrofurane and the exact equimolar amount of water was gradually added at or below 0 (cooling with ice–salt) After the exothermic reaction had subsided the mixture was allowed to warm up to room temperature, and stirring was continued for 0 5–1 hr After removal of the solvent the phosphonic fluoride was isolated by distillation *in vacuo*

Other phosphonic or phosphinic fluorides were isolated as by-products on the preparation of the corresponding fluorophosphoranes, while ethylphosphonic difluoride for example, was obtained on redistillation of a sample of ethyl tetrafluorophosphorane (b p 32–33), which was stored in a glass vial over a prolonged period (ca 6 months)

H *Fluorination with potassium bifluoride*

The P—Cl compound was stirred with an excess of the fluorinating agent in refluxing benzene

Remarks on the aromatic dichlorophosphination

a *Preparations* In the preparation of aromatic dichlorophosphines the procedure of BUCHNER and LOCKHART(20) was followed Boiling points and refractive indices were found in agreement with the reported data It may be noted that on the preparation of isopropyl-phenyldichlorophosphine some dealkylation occurred, phenyldichlorophosphine being among the products identified A similar observation has been made in the preparation of ethylphenyldichlorophosphine(9)

The tolyldichlorophosphine more closely investigated had b p 99 /5 mm, n_D^{20} 1 5901 n_D^{22} 1 5880, n_D^{27} - 1 5871 The yield was between 65–70 per cent A slight difference in composition of the isomer mixture as reflected by a small change in refractive index on different preparations under essentially identical conditions was noted The lack of homogeneity of the product thus obtained was also indicated by comparison of its refractive index with the data for authentic *o*- and *p*-tolyldichlorophosphine(23,24) *o*, n_D^{20} 1 598, *p*, n_D^{20} 1 591, the impurity in the *p*-compound probably being the *m*- rather than the *o*-isomer, since the latter has a refractive index higher than pure *para*)

The preparation of aryl tetrafluorophosphoranes will be described elsewhere(10) B p $CH_3C_6H_4PF_4$ 44 /4 mm Tolylphosphonic dichloride was made from the tolyldichlorophosphine isomer mixture according to the directions of TOY(40), b p 161–164 18 mm n_D^{25} 1 5546 (reported n_D^{25} 1 5542) Fluorophosphoranes and phosphonic fluorides were hydrolysed by repeated evaporation with excess water on a steam-bath The mixture of the isomeric tolylphosphonic acids and the pure *p*-isomer were recrystallized from water, while the hydrolysis product from *m*-tolylphosphonic difluoride was dried over phosphorus pentoxide at 45°/0.1 mm for 24 hr after evaporation to dryness. The gummy solid thus obtained was dissolved in a small volume of benzene, decolorized with charcoal and recrystallized from 1:1 benzene-hexane to give white crystals.

---

(40) A D F TOY, *J Amer Chem Soc* **70**, 186 (1948)

b. *Vapour phase chromatography.* A Perkin Elmer Model 154 Analytical Gas Chromatograph (10 ft × 1/4 in. column) was used for the analytical work.

$C_6H_5PF_4$: at 156° (40 cm³ carrier gas (helium) per min): 1 peak at 14.5 min.

$C_6H_5POF_2$: at 152° (40 cm³ carrier gas/min), 1 peak at ca. 19.6 min, in accordance with a b.p. of ca. 185° vs. 135° for $C_6H_5PF_4$.

$CH_3C_6H_4PF_4$: at 155° (40 cm³ carrier gas/min), 2 peaks (approximate ratio 2:1–3:1) at 12 and 14.5 min, respectively.

$CH_3C_6H_4POF_2$: at 168° (40 cm³ carrier gas/min): 2 peaks (approximate ratio 2:1–3:1) at 24.2 and 31.1 min, respectively.

$(CH_3)_2CHC_6H_4POF_2$: at 156° (40 cm³ carrier gas/min): 2 peaks (approximate ratio 2:1–3:1) at 45 and 48 min, respectively. The isomer mixture has b.p. 118–119°/19 mm.

All runs were carried out on a diisodecyl phthalate column. The tolyldichlorophosphine was run at 175° on a di-isodecyl phthalate column and at 202° on a silicon oil column DC 200. The material could not be eluted under these conditions and some chemical change seemed to occur.

The preparative separation of the tolylphosphonic fluoride isomers was carried out on a gas chromatograph Autochrome 200 (Potomac Instruments Co., Springfield, Va.) with a silicon oil (20 per cent on fire brick) column 14 ft × 1 in.; temperature 154°C; flow rate of carrier gas ca. 600 cm³/min. Retention times of 95 min (*m*) and 110 min (*p*) were observed. The identification of the separated compounds (purity checked by analytical VPC) is described above.

J. Inorg. Nucl. Chem. 1963, Vol. 25, pp. 349 to 351. Pergamon Press Ltd. Printed in Northern Ireland

THE PREPARATION AND PROPERTIES OF PERTECHNETYL FLUORIDE, TcO_3F*

H. Selig and J. G. Malm
Chemistry Division, Argonne National Laboratory, Argonne, Illinois

(*Received* 10 *August* 1962)

Abstract—Pertechnetyl fluoride, TcO_3F, has been prepared for the first time in gram quantities by the reaction of fluorine with TcO_2 at 150 °C. Its properties are intermediate between those of MnO_3F and ReO_3F. It is a yellow solid which melts at 18.3 °C to a yellow liquid. The vapour-pressure is represented by the following equations: Solid (−8.78–18.28 °C): $\log_{10} p = 12.448 - (3239.4/T)$; Liquid (18.28–51.82 °C): $\log_{10} p = 8.417 - (2064.6/T)$. The boiling point extrapolated from vapour-pressure measurements is about 100 °C. TcO_3F is stable at room temperature and can be stored in nickel or monel containers. It is hydrolysed by water to pertechnetic and hydrofluoric acids.

ALTHOUGH permanganyl fluoride, MnO_3F, and perrhenyl fluoride, ReO_3F, have been known for some time,(1) the corresponding technetium compound has not yet been isolated. Some scanty evidence for its existence was advanced by SITES *et al.*(2) who discovered TcO_3F^+ peaks in the mass spectrum of a mixture of Tc_2O_7 and UF_4 heated to 160°. We have now succeeded in preparing TcO_3F in sufficient amounts to study some of its physical and chemical properties.

Pertechnetyl fluoride can be prepared by passing fluorine gas over TcO_2 at 150°. This result is somewhat surprising in view of the results of AYNSLEY *et al.*(3) who found ReO_2F_3 and $ReOF_5$ to be the major products in the reaction of fluorine with ReO_2. The volatile TcO_3F is easily trapped in a dry-ice cooled trap. A small amount of a white solid occurs as a byproduct. It is non-volatile at room temperature but can be distilled at about 150 °C. No attempts were made to identify this product at this time. However, it is probably another oxyfluoride of heptavalent technetium since it hydrolyses without forming a precipitate.

Pure TcO_3F forms yellow crystals which melt at 18.3 °C to a yellow liquid. The vapor pressures of solid and liquid TcO_3F were measured and given in Equations (1) and (2).

Solid TcO_3F (−8.78–18.28 °C)

$$\log_{10} p = (12.448 \pm 0.059) - \frac{(3239.4 \pm 16.3)}{T} \tag{1}$$

Liquid TcO_3F (18.28–51.82 °C)

$$\log_{10} p = (8.417 \pm 0.022) - \frac{(2064.6 \pm 6.5)}{T} \tag{2}$$

where T is in degrees Kelvin and pressures in mm Hg at 0 °C and standard gravity.

The calculated triple point from simultaneous solution of Equations (1) and (2) is 18.28° C, in good agreement with the directly observed value of 18.5°. The extrapolated boiling point is about 100° C. The heat of sublimation of the solid is 14,832 cal mole^{-1} and the heat of vaporization of the liquid is 9,453 cal mole^{-1}. The heat of fusion is 5377 cal mole^{-1}.

---

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

(1) A. ENGELBRECHT and A. V. GROSSE, *J. Amer. Chem. Soc.* **76**, 2042 (1954).

(2) J. R. SITES, C. R. BALDOCK and L. O. GILPATRICK, U.S.A.E.C., ORNL-1327 (1952).

(3) E. E. AYNSLEY, R. D. PEACOCK and P. L. ROBINSON, *J. Chem. Soc.* 1622 (1950).

The oxyfluoride is stable at room temperature in nickel or monel storage vessels, but attacks even dry Pyrex or quartz fairly rapidly. However, the vapours attack dry quartz rather slowly. With excess water TcO_3F hydrolyses to $HTcO_4$ and HF.

Upon reaction with excess fluorine gas at 400° and 4 atmospheres pressure, TcO_3F is converted quantitatively to TcF_6. This is also borne out by the fact that in an attempt to prepare the oxyfluoride by reaction of fluorine on TcO_2 in a closed system under the above conditions, TcF_6 was the only product formed.

The properties of TcO_3F are intermediate between those of MnO_3F and ReO_3F as shown in Table 1.

TABLE 1

	m p (° C)	b p (° C)	Colour
MnO_3F[2]	38	~60	Green
TcO_3F	18.3	~100	Yellow
ReO_3F[3]	147	164	Yellow

EXPERIMENTAL

Materials

TcO_2 was prepared by decomposing NH_4TcO_4 (obtained in solution from Oak Ridge) in a stream of dry nitrogen at 300° C. The fluorine gas (98.5 per cent pure) was obtained from the Pennsalt Corporation. It was additionally purified from HF by condensation in liquid nitrogen.

Preparation

TcO_3F was prepared by passing fluorine gas at 250 mm pressure over TcO_2 in a nickel tube at 150°. The volatile product was collected downstream in a nickel U-tube cooled in a trichloroethylene–dry-ice bath. It was further purified from HF and other volatile impurities by repeated sublimations in an all monel line as described elsewhere.$^{(4)}$ After purification the yield was obtained by PVT measurements assuming one Tc atom per molecule. Because of the radioactivity of technetium only small quantities of materials were handled. In a typical reaction 1.63 g of TcO_2 yielded 1.16 g of TcO_3F (56 per cent yield). Upon completion of the reaction, a gray residue of indefinite composition was found to remain in the boat. This residue turned red upon exposure to moist air.

Molecular weight determination

The molecular weight of the compound was determined by weighing quantities of the gas under conditions of known pressure, temperature, and volume in a nickel bulb fitted with a miniature valve. Weighings were made with an identical bulb used as a tare.

The results based on both the empty bulb weights before and after weighing with TcO_3F are given in Table 2. The uncertainty in the determination is due mainly to the increase in the weight of the bulb during measurement and the small vapour-pressure of the compound.

Chemical analyses

Weighed samples of TcO_3F were sealed in Pyrex flasks cooled with liquid nitrogen. Dilute NaOH was admitted through a break seal and the hydrolysis proceeded as the sample warmed to room temperature. A clear colourless solution was obtained.

The total acidity of the aqueous solution was determined by dissolving a weighed quantity of the oxyfluoride in a known excess of NaOH solution and backtitrating with HCl. TcO_3F should hydrolyse according to Equation (3)

$$TcO_3F + H_2O \rightarrow HTcO_4 + HF \qquad (3)$$

---

(4) B WEINSTOCK and J G MALM *J Inorg Nucl Chem* **2**, 380 (1956)

TABLE 2.—MOLECULAR WEIGHT DETERMINATION

Pressure (mm)	Weight of gas (mg)	Increase in bulb wt (mg)	Mol wt	
			Initial bulb wt	Final bulb wt
17.08	20.3	1.1	178	169
22.92	26.7	1.2	176	168
20.32	23.1	−0.1	168	168
			Ave 171 ± 4	(theoretical 166)

i.e. two equivalents of acid should form per mole of oxyfluoride hydrolysed. It was found that 0.935 mmoles of TcO_3F liberated 1.879 mequivalents of acid, in accordance with theory. It should be noted that the other two possible heptavalent oxyfluorides, TcO_2F_3 and $TcOF_5$, would liberate 4 and 6 equivalents of acid per mole, respectively.

Fluorine was determined by titration with Th^{4+} using sodium alizarin sulphonate as an indicator. Technetium was determined by counting aliquots in a calibrated PCC-10 counter. From the total weight, oxygen was determined by difference. Analyses on two different samples gave the following results: Total sample I: 174.2 mg, Found: Tc, 102.5 mg, F, 21.7 mg, O, 50.0 mg. Calc.: Tc, 103.8 mg, F, 20.0 mg, O, 50.3 mg. Tc:O:F = 1:3.02:1.10. Total sample II: 155.2 mg, Found: Tc, 90.0 mg, F, 19.5 mg, O, 45.6 mg. Calc.: Tc, 92.5 mg, F, 17.8 mg, O, 44.9 mg. Tc:O:F = 1:3.14:1.13.

Vapour-pressures

Vapour-pressure measurements were made on a one gramme sample in a quartz differential Bourdon gauge used as a null instrument. A description of this apparatus and its manipulation is described elsewhere.(5) The overall sensitivity of the gauge was ~0.02 mm Hg. The thermostatted bath was regulated to ±0.01°C as measured with a copper constantan thermocouple which had been calibrated against a NBS platinum resistance thermometer. The vapour-pressure equations were derived by the method of least squares. Equation (1) represents eighteen points and equation (2) thirty-nine points.

Melting point

The melting point of TcO_3F was measured in a thin-walled Kel-F capillary.

Acknowledgement—We wish to thank Miss E. M. Fox of this laboratory for performing the fluorine analyses.

---

(5) B. WEINSTOCK, E. E. WEAVER and J. G. MALM, *J. Inorg. Nucl. Chem.* **11**, 104 (1959).

J. Inorg. Nucl. Chem. 1963, Vol. 25, pp. 353 to 359. Pergamon Press Ltd. Printed in Northern Ireland

COMPLEX FORMATION BETWEEN ORGANIC THIO-ACIDS AND GERMANIC ACID

E. R. CLARK
College of Advanced Technology, Gosta Green, Birmingham, 4, England

(*Received* 3 *August* 1962)

Abstract—The reaction between some organic thio-acids and germanic acid in aqueous solution has been investigated. Conductivity studies show that germanic acid reacts with thioglycollic acid, 1-mercaptopropionic acid and thiomalic acid to form 1:2 complexes in solutions of acid pH value. Germanic acid does not complex with 2-mercaptopropionic acid. Potentiometric titration of the complex acids show that germanothioglycollic and germano-1-mercaptopropionic acid behave as dibasic acids with pK_1 values of 2.05 and 1.92 respectively in 0.1 M KCl and a ligand concentration of 0.02 M. Germanothiomalic acid behaves as a tribasic acid with pK_1 = 1.91 under the same conditions. The complex acids appear to be decomposed gradually as titration with alkali proceeds beyond pH 6.0.

Many compounds of transition metals are known where sulphur is bonded to the metal. Dithio-oxalates of nickel, palladium and platinum were described some time ago.[1] Thioethers may act as ligands, examples being $(Et_2S)_2PdCl_2$, and $C_2H_4(EtS)_2PdCl_2$. Nickel (IV) may be stabilized by organic thio-acids.[2] Thiocarbamide and ethylene thiocarbamide are known to stabilise the cuprous state through π bond formation. Copper is co-ordinated to sulphur in such compounds as $Na[Cu(S_2O_3)]$ and $(NH_4)_5[Cu(S_2O_3)_3]$.[3] Sulphur-containing ligands such as Me_2S, $(CH_2)_4$ S, $(H_2N)_2C=S$ can displace cycloheptatriene from $C_7H_8Mo(CO)_3$ to give sulphur complexes.[4]

Apart from sulphides, examples of compounds containing non-transitional elements where sulphur is directly bonded are very few. Antimony derivatives of mercapto acids have been reported.[5] More recently complexes of GeF_4 with sulphur donors have been prepared.[6] The reaction between germanic acid and various hydroxy acids has been investigated in detail.[7,8] Replacement of the hydroxyl group by HS gives a series of thio-acids whose complexing abilities have not hitherto been investigated. Four acids which are obtainable in a good state of purity were chosen for the study—two containing α-SH groups (thioglycollic acid and 1-mercaptopropionic acid), one containing a β-SH group (2-mercaptopropionic acid) and finally one containing an SH group which is α- to one —COOH group and β- to another —COOH (thiomalic acid).

---

[1] F. G. COX, W. WARDLAW, K. C. WEBSTER *J. Chem. Soc.* 1475 (1935).
[2] W. HIEBER and R. BRUCK *Naturwissenschaften* **36**, 312 (1949).
[3] G. SPACU and I. G. MURGULESCU *Chem. Zentr.* (i) 3422, (ii) 535 (1930); (i) 1426 (1931).
[4] F. A. COTTON and F. ZINGALES *Chem. and Industr.* 1219 (1960).
[5] YU-YUAN HSIEH *et al. Hua Hsueh Hsueh Pao* **23**, 105–11 (1957).
[6] R. C. AGGARURAL and M. ONYSZCHUK *Proc. J. Chem. Soc.* **20**, (1962).
[7] E. R. CLARK *J. Inorg. Nucl. Chem.* **21**, 366–74 (1961).
[8] E. R. CLARK, Ph.D. Thesis London (1960).

EXPERIMENTAL

Materials

Spectrographically-pure quartz-type GeO$_2$ (99 98 per cent) was used for all experiments Purities of the thio-acids as determined by titration were thioglycollic acid, 98 0 per cent, thiomalic acid, 99 4 per cent, 1-mercaptopropionic acid, 100 per cent, 2-mercaptopropionic acid, 100 per cent The racemic forms of thiomalic acid and 1-mercaptopropionic acid were used It was assumed that the only impurity in thioglycollic acid was water and no attempt at purification was made

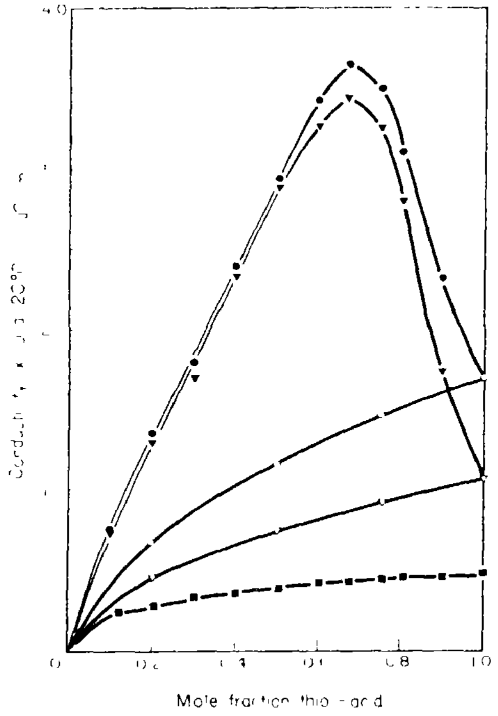


FIG 1 Conductivities of mixtures of 0 04 M Geo$_2$ and 0 04 M thio-acid ● thiomalic acid and Geo$_2$, thiomalic acid alone, ▼ thioglycollic acid and Geo$_2$ thioglycollic acid alone, ■ 2-mercaptopropionic acid and GeO$_2$ The curves for 1-mercaptopropionic acid and GeO$_2$ are almost identical with those of thioglycollic acid and GeO$_2$

Methods

Conductivity and pH studies The thio-acids of 0 04 M concentration were mixed in various molar proportions with 0 04 M solutions of GeO$_2$ The conductivities of these solutions were determined within four hours although experiments showed that solutions were stable for three weeks provided air was excluded The pH values of solutions of the germanothio-acids and the parent acids were also found to remain constant under the same conditions

The conductivities of the mixtures were determined by using a Mullard conductivity bridge and dip type cell All measurements were made at 20 C 0 1 C and are given in ohm^{-1} cm^{-1} (Fig 1)

Potentiometric titration A glass/calomel electrode system was used which was standardised with a BDH buffer of pH 4 0 The cell used for the potentiometric titrations has been described in a previous paper (9) Fifty ml aliquots of the germanothio-acids of ligand concentration 0 02 M in 0 1 M KCl were titrated with 0 348 N NaOH, the mixture being agitated by a flow of nitrogen gas The pH was measured after each successive 0 1 ml addition of NaOH Equilibrium was attained within 1 min The titrations were repeated on 50 ml samples of 0 02 M thio-acid and 0 1 M KCl

DISCUSSION AND RESULTS

The results of the conductivity experiments on mixtures of 0 04 M solutions of GeO$_2$ and 0 04 M thio acid are shown in Fig 1 Well defined maxima occur at molar fractions of 0 66 thio-acid for all thio-acids except 2-mercaptopropionic In the latter case the conductivities of mixtures of 2-mercaptopropionic acid and GeO_2 virtually coincide with the conductivities of the thio-acid alone (lower curve in Fig 1)

---

(9) E R CLARK, *J Inorg Nucl Chem* **24**, 81–91 (1962)

The results show that germanic acid forms 1 2 complexes with thioglycollic, 1-mercaptopropionic and thiomalic acids in aqueous solution Thio-acids containing β-SH groups evidently do not enter into complex formation The method of continuous variations as used here has been the subject of some criticism (10 11) Analysis of the potentiometric titration curves of the complex acids (Fig 2) indicates, however,

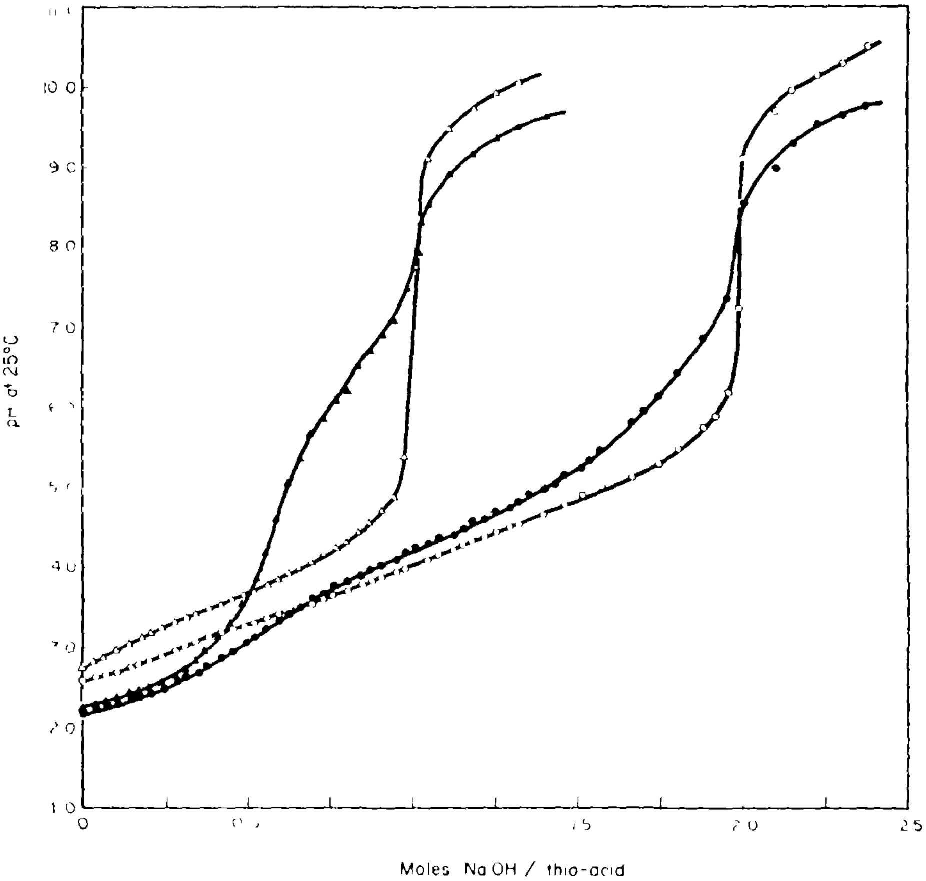


FIG 2 — Potentiometric titration curves for the complex thio-acids and the parent acids ● germanothiomalic acid, ○ thiomalic acid, ▲ germano-1-mercaptopropionic acid △ 1-mercaptopropionic acid The curves for germanothioglycollic and thioglycollic acid are similar to those of germano-1-mercaptopropionic acid and 1-mercaptopropionic acid respectively

that the Henderson equation is obeyed for the first part of all titration curves, indicating that only one species exists at lower pH values

The results of potentiometric titration of the complex acids are given in Fig 2 For germanothioglycollic and germano-1-mercaptopropionic acid neutralisation is clearly a two-stage process, the primary dissociation constant K_1 of the complex acid being larger and the second dissociation constant K_2 being smaller than that of the

(10) F WOLDBYE *Acta Chem Scand* **9**, 299–309 (1955)

(11) M M JONES, *J Amer Chem Soc* **81**, 4485 7 (1959)

parent acid. In the case of germanothiomalicacid the curve for the complex acid and the reference curve, i.e. that containing thiomalic acid alone, intersect at a mole ratio of NaOH/thio-acid of 0.66 which is one third of the way to neutralisation. This indicates that the titration of the complex acid is probably a three-stage process, the primary dissociation constant of the complex acid being greater and of subsequent stages being smaller than those of the parent acid.

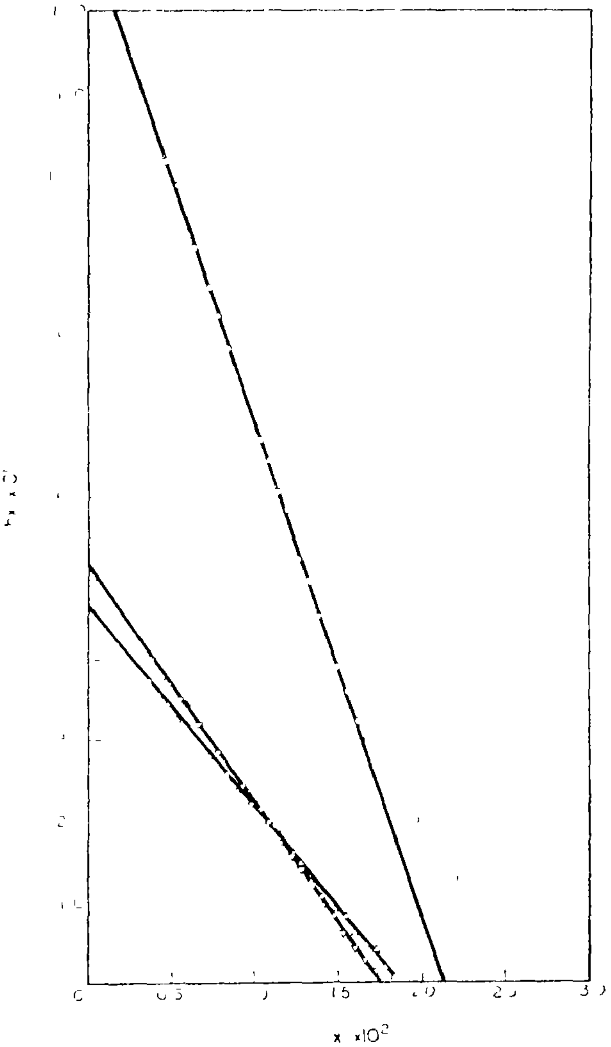


FIG. 3. Plot of 'hx' against 'x' for the parent acids. First stage titration, of thiomalic acid, thioglycollic acid, β-mercaptopropionic acid.

Analysis of the titration curves was carried out by the procedure recommended by GAGE[12]. The dissociation constants for the complex acid may be calculated by re-arranging the Henderson equation thus

$$hx = Kc - Kx$$

where K = the classical dissociation constant, c = total concentration of acid, $x = a + h - K_W/h$ where a = concentration of added alkali, h = hydrogen ion concentration, K_W/h = hydroxyl ion concentration. The plot of hx against x should be a straight line of slope K. Figure 3 shows the results for the parent acids, pK values are given in Table 1.

---

[12] J. C. GAGE, *Analyst* **82**, 219 (1957).

Figure 4 shows the plots of hx against x for the first stages of titration of the germanothio-acids and the corresponding pK values are given in Table 1. Deviation from

TABLE 1

	pK_1	pK_2	pK_3
Thioglycollic acid	3.50	—	—
1-mercaptopropionic acid	3.61		
Thiomalic acid	3.22	4.69	—
	3.25*	4.57*	—
Germanothioglycollic acid	2.05	5.40	
Germano-1-mercaptopropionic acid	1.92	5.70	—
Germanothiomalic acid	1.91	4.40	5.50

* By SPEAKMAN's method(11) activity coefficients taken as 1.

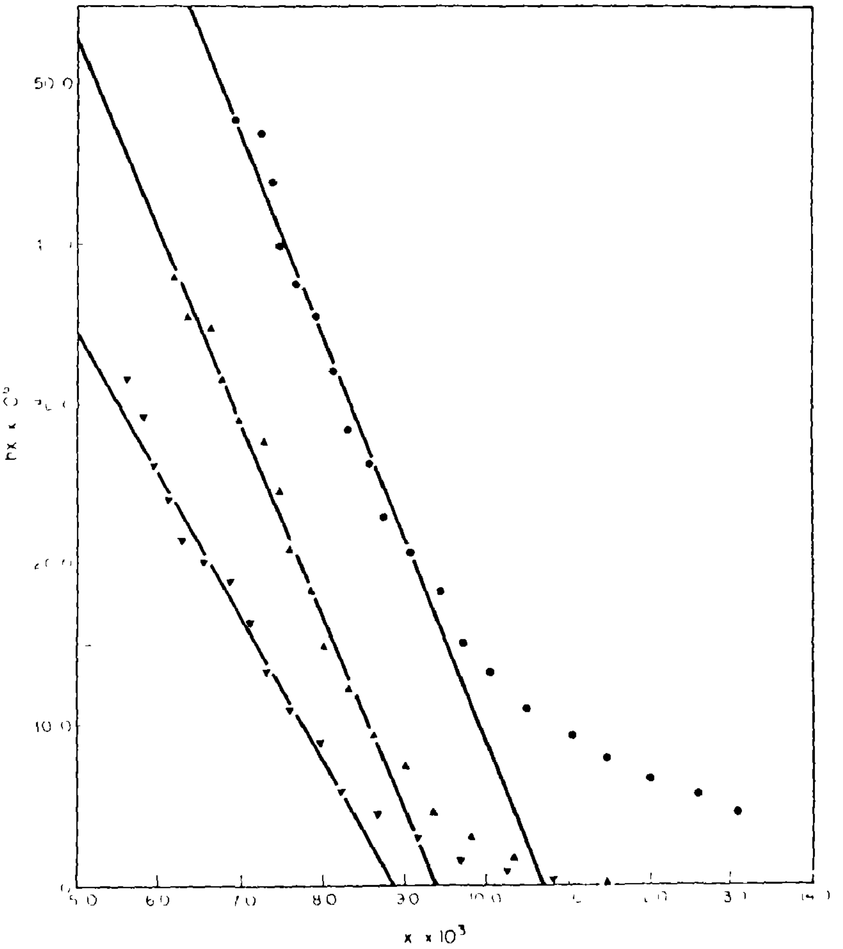


FIG. 4. Plot of "hx" against "x" for the complex acids. ● First stage of titration of germanothiomalic acid, ▼ first stage of titration of germanothioglycollic acid, ▲ first stage of titration of germano-1-mercaptopropionic acid.

(11) J. C. SPEAKMAN, *J. Chem. Soc.* 855–9 (1940).

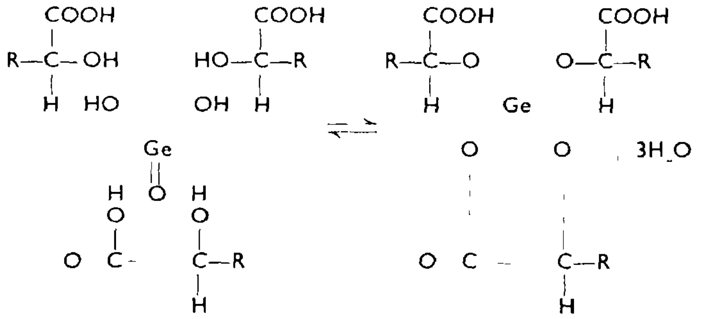
the straight line relationship occurs towards the end of each stage and in this region it is possible that hydrogen ions from the second stage are being replaced before the first stage is complete Application of the Speakman[13] method does not give straight line graphs, however, and it may be inferred that some decomposition must occur during the second stages The plot of h/x against x shows a straight line relationship only for the central portion of each plot Thus values for pK_2 and pK_3 for the germanothio-acids in Table 1 are only approximate since it is considered that some decomposition occurs around pH 6 in each case

Comparison of the results for the germanothio-acids with those of the corresponding germanohydroxy acids[8, 9] shows that

(1) replacement of the oxygen in OH by the more easily polarisable sulphur gives a complex acid with fewer attached ligands, i e germanic acid forms 1 3 complexes with glycollic and malic acids but with thio-glycollic and thiomalic 1 2 complexes are formed The reactions between germanic acid and an organic hydroxy acid may be written thus

$$H_2GeO_3 \quad 3H_2L \quad GeL_3^{2-} \quad 2H^+ \quad 3H_2O$$

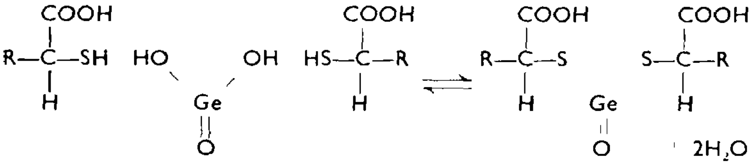
or more fully



For the thio-acids

$$H_2GeO_3 \quad 2H_2L \quad GeL_2^{2-} + 2H^+ + 2H_2O$$

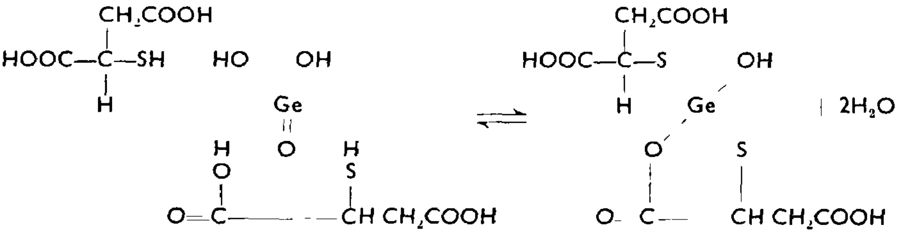
or



Thus for the thio-acids the hydroxy of the carboxylic group need not be involved in the reaction However, the case of thiomalic acid is interesting in that this acid contains one —COOH α- to the SH and one β- to the SH and yet the complex acid is tribasic Presumably one of the —COOH groups enters into complex formation

$$H_2GeO_3 + 2H_3L \quad [HO\,GeL_2]^{3-} + 3H^+ + 2H_2O$$

or



(2) Even though the number of ligands is fewer when sulphur is involved the basicity of the complex acids is the same, i e both germanothioglycollic and germanoglycollic acid are dibasic and germanothiomalic and germanomalic acid are tribasic

(3) The germanothio-acids are stronger acids than the corresponding germanohydroxy acids, cp pK_1 germanoglycollic 3 73 in 0 1 M KCl, pK_1 for germanothioglycollic 2 05 under same conditions

J. Inorg. Nucl. Chem. 1963. Vol. 25. pp. 361 to 363. Pergamon Press Ltd. Printed in Northern Ireland

CONDUCTOMETRIC AND SPECTROPHOTOMETRIC STUDY OF THE SYSTEM MANGANESE CHLORIDE-SALICYLOYL HYDRAZIDE

M. S. Kachhawaha and Arun K. Bhattacharya
Department of Chemistry, University of Saugar, Saugor, (M.P.) India

(*Received* 23 *August* 1961; *in revised form* 6 *September* 1961)

Abstract—Conductometric and spectrophotometric methods show that manganous chloride and salicyloyl hydrazide form a 1 : 1 complex; the dissociation constant is 9.7×10^{-4} at 26°C. A structure for the complex is suggested.

Reactions of salicylic acid and its various derivatives with an appreciable number of metals, especially those of the transitional groups,⁽¹⁻⁵⁾ have been studied by physico-chemical methods, and it has been observed that the above ligands generally behave as strong complexing agents. With the exception of the manganous salicylaldehyde complex⁽⁶⁾ there is little information on the reactions of salicylic acid and its derivatives with manganous ion. The present communication deals with a conductometric and spectrophotometric study of the manganese (II) salicyloyl hydrazide complex by Job's method⁽⁷,⁸⁾; only a few complexes of the latter have been reported previously.⁽⁹⁾

EXPERIMENTAL

A mixture of 30.4 g of methyl salicylate and 14.7 g of hydrazine hydrate were mixed together and refluxed on a water bath for about 2½ hr. The product was then cooled, and the pink solid mass crystallized twice from hot water (m.p. 146.5°C, in agreement with the reported value.)

A 10 per cent solution of dioxan (BDH) in water was utilized as a solvent as salicyloyl hydrazide is insoluble in water. Job's method was utilized to determine both the composition and the dissociation constant of the complex. Measurements of optical density as a function of wavelength for mixtures of three different compositions (1 : 1, 1 : 2 and 1 : 3) indicated maxima at 240 mμ and 300 mμ irrespective of composition, indicating the formation of a 1 : 1 complex.

Composition of the complex

A set of mixtures was prepared from equimolar solutions keeping the volume constant at 20 ml. Two blank solutions of the metal and ligand were prepared corresponding to every mixture. The electrical conductance of the mixtures and corresponding blank solutions was measured and the

---

(1) Babko, *J. Gen. Chem.* **17**, 443 (1947); *Zavodskaya Lab.* **13**, 645 (1947).

(2) Mehrotra and Verma, *J. Indian Chem. Soc.*, **39**, 381–90 (1958).

(3) Bands and Patterson, *J. Amer. Chem. Soc.* **73**, 3062 (1951).

(4) M. S. Kachhawaha and Arun K. Bhattacharya, *Proc. Nat. Acad. Sci.* **29** (IV) A, 315–319 (1960).

(5) Arun K. Bhattacharya *et al.*, *J. Sci. Ind. Res.* **18** (B), 351 (1959).

(6) Martell and Mellor, *Nature*, **165**, 453, 1950; *Ann. Chim.* X(9) 113.

Job, *C. R. Acad. Sci., Paris*, **180**, 928 (1925).

M. S. Kachhawaha and Arun K. Bhattacharya, *Z. Anorg. Chem.* **315**, 104 (1962).

Jabalpurwala, Ph.D. thesis, University of Bombay, India (1960).

difference in conductance divided by the sum of the conductivities of the corresponding blank solutions was plotted against the composition of the mixtures. It was found that, irrespective of the concentrations, the maxima corresponded to the formation of a 1 : 1 complex. A spectrophotometric study using M/1000 solutions of both reagents showed the composition to be the same and it was found that at the wavelengths 220, 240 and 500 mμ.

Dissociation constant

The same procedure was adopted except that the solutions were not equimolar. The dissociation constant was determined from the general formula for a 1 : 1 complex, viz.

$$K = \frac{C[(p-1)(x-1)]^2}{(p-1)(1-2x)}$$

where

K = dissociation constant

C = concentration of metal ion

p = ratio of the concentrations of metal and ligand

x = fraction of the ligand present in the equilibrium mixture corresponding to the maxima in the curves.

K was found to be 9.7×10^{-5} at 26 ± 0.1°C (Fig. 1).

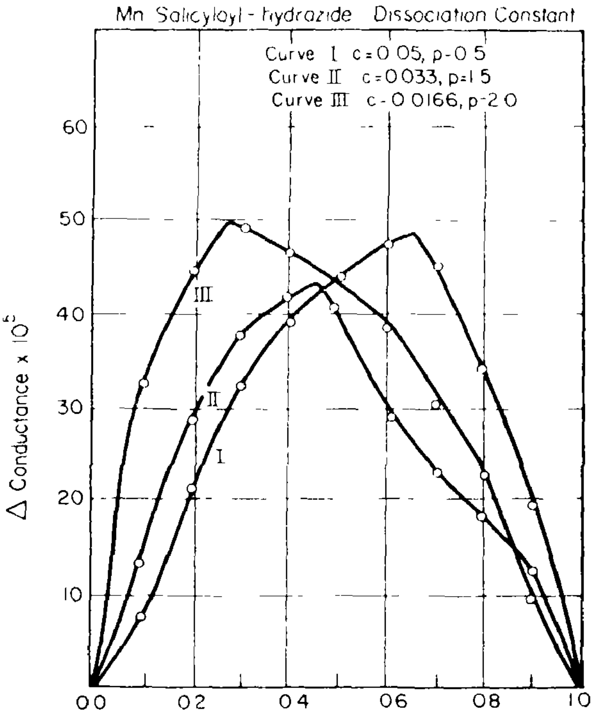


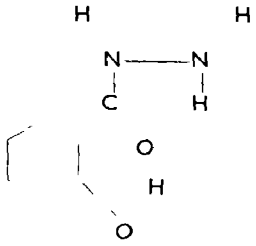
FIG. 1

Structure of the complex

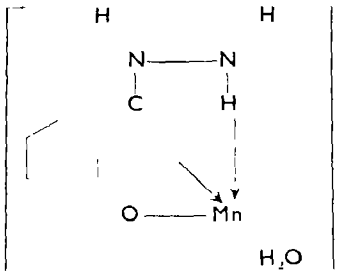
The metal ion may be expected to co-ordinate with the basic group as in the case of copper ammoniate. It has been found by earlier workers[10] that the protons attached to the basic nitrogen are displaced at the same time as the phenolic proton, and the structure of salicyloyl hydrazide, viz

---

[10] BRAUDE and NACHOD, *Determination of Organic Structures by Physical Methods* p. 644 Academic Press New York (1955).



indicates the possibility of forming an additional hydrogen bond besides that embracing the ketonic oxygen and the phenolic hydrogen This would cause the phenolic hydrogen to be less strongly held by the ketonic oxygen, and hence the phenolic hydrogen will be more readily ionized, leading to complex formation between the phenolic oxygen and the ketonic oxygen The following structure therefore seems to be a likely one



Acknowledgment The authors wish to express their gratitude to Professor A K BHATTACHARYA for his valuable suggestions from time to time

J. Inorg. Nucl. Chem. 1963. Vol. 25, pp. 365 to 368. Pergamon Press Ltd. Printed in Northern Ireland

A PREPARATIVE STUDY OF THE REACTION BETWEEN ANTIMONY(III) BROMIDE AND AMINE HYDROBROMIDE COMPOUNDS*

R. D. **Whealy** and R. L. **Yeakley**†‡
Department of Chemistry, Agricultural and Mechanical College of Texas,
College Station, Texas

(*Received* 24 *April* 1961; *in revised form* 10 *August* 1962)

Abstract—The reactions between antimony tribromide and twenty amine hydrobromides were studied. The complex compounds formed were recrystallized, analyzed for bromine and antimony content, their melting points and qualitative solubilities were determined. Analytical results indicated fifteen of the complex compounds had bromine to antimony ratios of 5 to 1, four of the compounds had bromine to antimony ratios of 6 to 1, one of the compounds had bromine to antimony ratio of 9 to 2.

The synthesis of compounds of the type $R_xSb_yBr_z$, where R represents either an aliphatic or aromatic amine, has been known since Rosenheim and Stellman[1] reported the preparation of $(C_5H_5NH)_2SbBr_7$ from the reaction of pyridine hydrobromide and antimony(III) bromide in an acid solution saturated with bromine water. The same general procedures with minor variations were followed by Weinland[2], Ephraim,[3] Petzold,[4] Hays,[5] Caven,[6] Brauer[7] and Lamchen[8] with a wide variety of types of compounds reported: (1) $RSbBr_4$ (2) $RSbBr_6$ (3) $RSbBr_7$ (4) R_2SbBr_5 (5) R_2SbBr_6 (6) R_2SbBr_7 R_2SbBr_8 (8) R_2SbBr_9 (9) R_3SbBr_6 (10) $R_3Sb_2Br_9$ (11) $R_3Sb_2Br_{11}$ (12) $R_3Sb_2Br_{12}$ (13) $R_3Sb_2Br_{15}$ (14) $R_5Sb_3Br_{14}$ (15) $R_7Sb_3Br_{16}$ (16) $R\,SbBr_3 \cdot 3HBr$. Vournazous[9] dissolved a number of solid bromide salts in an acetone solution of antimony(III) bromide. He isolated a number of complex compounds which had the general formula $A_2Sb_3Br_{11}$ in which A represents an alkali metal ion.

EXPERIMENTAL

Materials

Antimony tribromide was prepared from reagent grade antimony trioxide. Most of the amines were white label Eastman chemicals and were used without further purification. All solvents were reagent grade.

Procedure

The antimony(III) bromide solutions were prepared by dissolving reagent grade antimony trioxide in an excess of hot hydrobromic acid. This solution was made to definite volume and aliquot portions used in the individual syntheses. The amine hydrobromides were prepared by adding an excess of hydrobromic acid to the amine. The salts were not isolated and sufficient 95 per cent ethanol was added to dissolve any salt precipitate. The water content of the solutions was held to a minimum since the desired products tend to decompose in dilute aqueous solutions. Approximately ten moles of the amine hydrobromide was added for each mole of the antimony (III) bromide used in each case. The complex salts usually formed immediately and in all cases precipitation was complete in a short time. The resulting crystals were separated by vacuum filtration through a Buchner funnel and rinsed first with isopropanol and then with diethyl ether. The compounds were recrystallized from isopropanol or acetone and diethyl ether was used when necessary to induce precipitation. The products were washed with diethyl ether and dried in a vacuum desiccator.

---

* This work was partially supported by the U.S. Army Research Office, Durham.

† Recipient of employee financial aid from the Dow Chemical Company for graduate study.

‡ Present address: Texas Instrument Company, Dallas, Texas.

[1] A. Rosenheim and W. Stellman, *Ber. Chem. Dtsch. Ges.* **34**, 3377 (1901).

[2] R. F. Weinland and C. Feige, *Ber. Chem. Dtsch. Chem.* **36**, 244 (1903).

[3] F. Ephraim and S. Weinberg, *Ber. Chem. Dtsch. Chem.* **42**, 4477 (1909).

[4] W. Petzold, *Z. Anorg. Chem.* **215**, 92 (1933).

[5] J. A. Hays, *J. Amer. Chem. Soc.* **24**, 360 (1902).

[6] R. M. Caven, *Proc. Chem. Soc.* **21**, 187 (1905).

[7] G. Brauer and W. D. Schnell, *Z. Anorg. Chem.* **287**, 87 (1956).

[8] M. Lamchen, W. Pugh and A. M. Stephen, *J. Chem. Soc.* 4418 (1954).

[9] A. Ch. Vournazous, *Z. Anorg. Chem.* **192**, 369 (1930).

Physical properties of the compounds

The compounds are all yellow, varying somewhat in shade and the variation in shade does not seem to be related directly to the fraction of antimony in the compounds. The compounds are probably soluble in water but apparently undergo an immediate decomposition forming SbOBr which precipitates. They are quite soluble in methanol, less soluble in ethanol, acetone and isopropanol. The compounds are only slightly soluble in diethyl ether and insoluble in chloroform, carbontetrachloride, benzene and petroleum ether. Their solubility seems to be directly proportional to the dielectric constant of the solvent. All of the compounds melted over a rather small range except bis-piperidiniumpentabromoantimonate(III) and 1,6-hexane-diammoniumpentabromoantimonate (III) which decomposed at a temperature of about 280° C. The melting point temperatures are shown in Table 1.

Analytical procedure and results

The antimony was determined by oxidation with iodine solution which had been standardized with primary standard arsenious oxide. The samples were dissolved in a 10 per cent tartaric acid solution and buffered with a saturated solution of sodium bicarbonate. A starch solution was added as the indicator. The bromine content of the compounds was determined by titration with silver nitrate which had been standardized using primary standard sodium chloride. The end point was determined potentiometrically using a silver indicator electrode with a mercury-mercurous sulphate reference electrode. The results of the analysis are shown in Table 1.

DISCUSSION

MOELLER(10) says that antimony forms either tetrahedral, square planar, or octahedral coordinate compounds, the latter being the most common. At the initiation of this work it was assumed the bromine to antimony ratio would be 4 to 1 or 6 to 1 in the expected products. Fifteen of the compounds prepared gave analysis which indicated a 5 to 1 ratio of bromine to antimony. All of these compounds had small melting point ranges except two which decomposed at relatively high temperature. One compound tris-di-ethylammoniumhexabromoantimonate(III) was prepared in relatively high purity and had a short melting point range. The reaction of di-n-propylammonium hydrobromide with antimony(III) bromide resulted in a compound for which the analytical results indicated it to be tris-di-n-propylammoniumhexabromoantimonate(III). This material gave substantially the same analysis upon repeated recrystallizations but always had a very wide melting point range.

The existence of pentabromo antimony complexes is not a necessary corollary of analytical results of solid materials which show a 5 to 1 bromine to antimony ratio. There are at least five possible explanations of these results only two of which involves a pentabromo complex.

(1) The complex ion could be in the form of a trigonal bipyramid.

(2) analytical results would not distinguish between R_2SbBr_5 and $R_4Sb_2Br_{10}$. The $R_4Sb_2Br_{10}$ compound would have two octahedra with antimony atoms at the center with bromine atoms at the corners of the octahedra with two bromine atoms shared by the antimony atoms.

---

(10) T. MOELLER, *Inorganic Chemistry: An Advanced Textbook*, p. 269. J. Wiley and Sons, New York (1952).

TABLE 1

	m.p. Range °C	Antimony (%)		Bromine (%)	
		Theoretical	Experimental	Theoretical	Experimental
$(C_5H_{11}NH_3)_2SbBr_5$	194–196	17.45	17.45 ± 0.02	57.27	56.97 ± 0.05
$(C_6H_5CH_2NH_3)_2SbBr_5$	197–198	16.48	16.26 ± 0.04	54.08	54.18 ± 0.02
$(CH_3(CH_2)_2CH_2NH_3)_2SbBr_5$	214.5–215.5	18.18	18.00 ± 0.01	59.67	59.21 ± 0.02
$[(CH_3)_2CHCH_2NH_3]_2SbBr_5$	223–224	18.18	17.76 ± 0.02	59.67	59.09 ± 0.28
$(C_6H_{11}NH_3)_2SbBr_5$	252–255	16.87	16.90 ± 0.03	55.37	55.35 ± 0.02
$(CH_3\ CH(CH_3)CH_2CH(CH_3)NH_3)_2SbBr_5$	211.5–212	16.78	16.48 ± 0.01	55.06	54.56 ± 0.05
$(C_2H_5NH_3)_2SbBr_5$	245.5–247.5	19.85	19.37 ± 0.03	65.13	64.90 ± 0.10
$(CH\ CH\ CH\ CH\ C(CH_3)\ NH)_2SbBr_5$	103.5–108	17.16	17.18 ± 0.01	56.31	56.15 ± 0.01
$(CH\ CH\ CH\ C(CH_3)\ CH\ NH)_2SbBr_5$	151.5–152	17.16	17.13 ± 0.01	56.31	56.50 ± 0.04
$(CH\ CH\ C(CH_3)\ CH\ CH\ NH)_2SbBr_5$	158–158.5	17.16	17.08 ± 0.02	56.31	55.85 ± 0.03
$[(CH_2)_5NH_2]_2SbBr_5$	d. 281	17.55	17.36 ± 0.01	57.61	57.12 ± 0.24
$(CH_3(CH_2)_2NH_3)_2SbBr_5$	229–230	18.98	18.90 ± 0.03	62.28	61.99 ± 0.15
$((CH_3)_2CHNH_3)_2SbBr_5$	244–245	18.98	18.88 ± 0.04	62.28	62.14 ± 0.17
$(C_5H_5NH)_2SbBr_5$	243–244	17.87	17.83 ± 0.04	58.63	58.62 ± 0.06
$H_3N(CH_2)_6NH_3SbBr_5$	d. 283	19.04	18.87 ± 0.01	62.48	62.23 ± 0.01
$((C_2H_5)_2NH_2)_3SbBr_6$	165.5–166.5	14.78	14.86 ± 0.03	58.21	57.67 ± 0.22
$((C_3H_7)_2NH_2)_3SbBr_6$	130–194	13.41	13.48 ± 0.01	52.82	52.72 ± 0.10
$((C_4H_9)_2NH_2)_3SbBr_6$	106–212	12.28	12.65 ± 0.01	48.34	48.31 ± 0.17
$((CH_3)_2CH)_2NH_2)_3SbBr_6$	150–210	13.41	13.74 ± 0.02	52.82	52.68 ± 0.20
$(CH_3NH_3)_3Sb_2Br_9$		23.14	23.11 ± 0.01	67.72	67.64 ± 0.13

(3) BYSTROM and WILHELMI[11] reported a study of a series of antimony fluoride complex compounds similar to ones reported in this paper. From X-ray diffraction studies they concluded that the SbF_5 group existed as a regular octahedron with the fluorine atoms at five corners and an unshared pair of electrons at the sixth position.

(4) The compounds could be double salts composed of tetra coordinated antimony and bromine with one mole of amine hydrobromide.

(5) The solids obtained were mixtures of the tetra coordinated complex and amine hydrobromide salts. The consistent analytical data obtained on repeated recrystallization of these materials would seem to make the fifth alternative very improbable if not impossible.

Since the systematic syntheses of compounds which had a 5 to 1 bromine to antimony ratio was unexpected, an attempt was made to carry out a series of reactions under quite different conditions. The reaction of cyclohexyl amine with antimony(III) bromide was used because it seemed to be the compound most easily made in high purity. The four different procedures were:

(1) the amount of amine hydrobromide required to form the tetrabromo compound was used.

(2) three times the amount required to give the pentabromo compound was used,

(3) ten times the amount required to give the pentabromo compound was used and the amine salt was added to the antimony(III) bromide,

(4) ten times the amount required to give the pentabromo compound was used but the antimony(III) bromide was added slowly with stirring to the amine hydrobromide salt solution.

After the same washing and drying procedures the product of the four different procedures had the same melting points and identical analytical results within the limit of experimental error. The only variation was in the amount of product which increased as the amount of amine hydrobromide salt was increased. Attempts to prepare the pentabromo compounds using di-n-propylamine and di-isopropyl-amine by decreasing the ratio of amine salt to antimony(III) bromide were unsuccessful. The decreased amount of salt merely decreased the amount of product but always gave the hexabromo compound.

---

[11] A. BYSTROM and K. WILHELMI, *Arkiv Kemi* 3, 461 (1952).

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 369 to 375. Pergamon Press Ltd. Printed in Northern Ireland

THERMODYNAMICS OF SOLUTION OF SOME INNER COMPLEX SALTS—II

M. M. Jones, A. T. Davila, J. F. Hix, Jr. and R. V. Dilts
Department of Chemistry, Vanderbilt University, Nashville 5, Tennessee

(*Received* 18 *June* 1962)

Abstract—The solubilities of chromium(III) acetylacetonate, uranyl acetylacetonate monohydrate, and the uranyl oxinate complex containing an additional molecule of oxine have been determined in several solvents over a range of temperatures. These solutions appear to conform approximately to Hildebrand's criteria for regular solutions. The solubility parameters of these complexes have been evaluated, and the thermodynamic functions for the solution processes have been calculated. The constancy of the solubility parameters toward various solvents suggests the possibility of prediction of the solubilities of these materials in non-polar solvents. The molal volumes of solutions of some highly symmetrical octahedral complexes in benzene are found to be represented very accurately by a linear equation in terms of mole fraction. The prediction of solubility parameters from the structural features of the inner complex salts is possible by the extension of Small's procedure for organic compounds.

In an earlier paper,[1] reporting measurements of the solubilities of a number of inner complex salts in a variety of solvents, it was suggested that the data could be systematized by the use of the concept of the "regular solution" as introduced and expounded by Hildebrand.[2,3] This present work had three goals: first, to extend this treatment to some other types of inner complex salts, second, to examine the partial molal volume of the solute with respect to concentration for some of these solutions, and third, to establish whether or not these solutions were sufficiently regular to enable the prediction of the solubilities of inner complex salts in various non-polar solvents.

EXPERIMENTAL

Materials. The chromium(III) acetylacetonate was obtained from the Mackenzie Chemical Works, Central Islip, Long Island, N.Y. The cobalt(III) acetylacetonate was prepared and purified using the method given in *Inorganic Syntheses*.[4] The uranyl oxinate containing an extra molecule of oxine was prepared by the method of van Tassel and Wendlandt[5], and the uranyl acetylacetonate monohydrate was obtained by a modification of the method of Biltz and Clinch.[6] This modification consisted of the slow addition of a solution of sodium bicarbonate to a rapidly stirred solution containing uranyl nitrate and an excess of acetylacetone, until the pH of the solution reached 7.5. The precipitate which had formed was collected and dried in air. This product, analyzed for its uranium content by ignition to U_3O_8, was found to contain 41.01% U, which compares favourably with the theoretical value of 40.68 per cent.

The solvents used for a large part of this work were of reagent or C.P. grade and were used without further purification, except for the benzene used in the study of the partial molal volumes of $Co(C_5H_7O_2)_3$ and $Cr(C_5H_7O_2)_3$. This was purified by distillation and the material used had a refractive index of 1.4970 at 27.4°. Timmermans[7] gives a refractive index of 1.4979 for the pure solvent at 25°.

---

[1] M. M. Jones, J. L. Wood and W. R. May, *J. Inorg. Nucl. Chem.* **23**, 305 (1961).

[2] J. H. Hildebrand and R. L. Scott, *The Solubility of Nonelectrolytes*. Reinhold, New York (1950).

[3] J. H. Hildebrand and R. L. Scott, *Regular Solutions*. Prentice-Hall, Englewood Cliffs, N.J. (1962).

[4] B. E. Bryant and W. C. Fernelius, *Inorganic Syntheses* (Edited by T. Moeller) Vol. V, p. 188. McGraw-Hill, New York (1957).

[5] J. H. van Tassel and W. W. Wendlandt, *J. Amer. Chem. Soc.* **81**, 813 (1959).

[6] W. Biltz and J. A. Clinch, *Z. Anorg. Chem.* **40**, 221 (1904).

[7] J. Timmermans, *Physico-Chemical Constants of Pure Organic Compounds* p. 147. Elsevier Publishing Co., Amsterdam (1950).

Methods. The solubilities of the inner complex salts were determined using the modified Alexieff procedure described earlier.(1) The densities of the solid complexes and the densities of their solutions used in the determination of the partial molal volumes were determined pycnometrically.(8) Robertson pycnometers were used for the solution density determinations. These latter solutions were analysed following the density determinations by evaporating the solvent carefully from a known weight of the solution and weighing the residual solute.

RESULTS AND DISCUSSION

The solubilities of the inner complex salts investigated in various solvents at varying temperatures are presented in Tables 1–4. The densities and partial molal volumes for chromium(III) acetylacetonate and cobalt(III) acetylacetonate in benzene are given in Table 5. When the solubility data is plotted, log x_2 vs. T^{-1}, it is found that the temperature variation changes slope in a few cases. This effect is usually indicative

TABLE 1.—SOLUBILITIES OF $Cr(C_5H_7O_2)_3$ IN MOLE FRACTION

Solvent	Temperature (°K)							
	298		303		308		313	
Benzene	7.25	10	7.54	10^{-}	8.22	10^{-}		
Carbon tetrachloride	2.75	10^{-}	2.99	10^{-}	3.49	10		
Chloroform	2.99	10	3.74	10^{2}	4.53	10^{-}		
Cyclohexane	2.95	10^{1}	3.69	10^{1}	5.01	10^{1}	6.08	10^{1}
p-xylene	1.64	10^{2}	1.75	10^{2}	1.83	10^{2}	2.30	10^{-}
Toluene	1.47	10^{2}	2.51	10^{-}	4.05	10^{-}	4.11	10^{2}
N-Heptane	2.47	10^{1}	3.07	10^{4}	6.62	10^{1}	8.28	10^{1}

The solubilities of $Cr(C_5H_7O_2)_3$ in benzene, carbon tetrachloride, and chloroform are from the first paper in this series.

TABLE 2.—SOLUBILITIES OF $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$ IN MOLE FRACTION

Solvent	Temperature (°K)							
	298		303		308		313(311)	
Benzene	1.88	10	2.71	10	3.28	10	6.26	10
Carbon tetrachloride	3.85	10	5.55	10	6.84	10	5.50	10
Chloroform	8.98	10	1.13	10^{1}	1.43	10^{1}	1.63	10^{4}
Cyclohexane	3.39	10	3.20	10	3.80	10	4.37	10^{5}
p-xylene	5.23	10	6.54	10	9.27	10	1.06	10^{4}
Toluene	3.10	10	4.03	10	4.33	10	(4.67	10)
N-heptane	2.08	10	3.47	10	4.49	10	5.45	10^{5}

TABLE 3.—SOLUBILITIES OF $UO_2(C_5H_7O_2)_2 \cdot H_2O$ IN MOLE FRACTION

Solvent	Temperature (°K)							
	298		303		308		313(311)	
Benzene	7.42	10^{1}	7.85	10^{1}	7.85	10^{1}	9.50	10^{1}
Carbon tetrachloride	5.34	10	9.23	10	1.21	10^{1}	1.81	10^{1}
Chloroform	7.45	10^{1}	1.04	10	1.50	10	1.51	10^{3}
Cyclohexane	2.60	10	3.96	10^{5}	4.84	10^{5}	6.89 ×	10
p-xylene	3.88	10^{4}	4.71	10^{1}	5.50 ×	10^{1}	5.34 ×	10^{4}
Toluene	3.67	10^{4}	4.79	10^{4}	5.95 ×	10^{1}	(5.87 ×	10^{4})
N-heptane	4.22	10	4.22	10^{6}	6.65	10^{5}	7.83	10^{6}

---

(8) J. REILLY and W. N. RAE, *Physico-Chemical Methods*, 4th Ed., Vol. 1, p. 474. Van Nostrand, Princeton, N.J., (1953).

TABLE 4 — SOLUBILITY OF $Co(C_5H_7O_2)_3$ IN BENZENE

T (°K)	Mole fraction solubility $\times 10^2$
283	2.656
288	2.884
293	3.045
298	3.197
303	3.374
308	3.627
313	3.978
318	4.245

TABLE 5 — DENSITIES AND MOLAL VOLUMES OF BENZENE SOLUTIONS OF $Cr(C_5H_7O_2)_3$ AND $Co(C_5H_7O_2)_3$

$Cr(C_5H_7O_2)_3$		$Co(C_5H_7O_2)_3$	
$n_2 \times 10^2$	ρ	$n_2 \times 10^2$	ρ
0	0.86829		
0.8029	0.87936	0.2896	0.87224
1.2960	0.88402	0.3750	0.87351
1.8234	0.89034	0.4603	0.87465
2.1945	0.89454	0.5399	0.87578
2.5923	0.89950	0.6044	0.87675
3.0675	0.90481	0.6779	0.87771
3.5019	0.90967	0.8188	0.87988
3.8926	0.91350	0.9171	0.88123
4.3297	0.91861	1.0253	0.88248
4.7357	0.92301	1.0987	0.88349
5.0732	0.92743	1.2847	0.88638
5.4521	0.93155	1.3849	0.88798
5.9517	0.93528	1.6418	0.89131
6.3700	0.93942	1.7506	0.89267
6.7440	0.94324	1.8952	0.89443
7.1816	0.94765	2.0026	0.89614
		2.1195	0.89767
		2.2109	0.89907
		2.2127	0.89898
		2.3253	0.90018
		2.4234	0.90143

$Cr(C_5H_7O_2)_3$	$Co(C_5H_7O_2)_3$
$v = 89.946 + 181.48n_2$	$v = 89.987 + 169.81n_2$
$\sigma = 0.051$	$\sigma = 0.019$
$\left(\frac{dv}{dn_2}\right) = \bar{v}_2 = 181.48$	$\left(\frac{dv}{dn_2}\right) = \bar{v}_2 = 169.81$

of a change in the composition or structure of the solid phase. This variation in the slope was most frequently observed in the case of the uranium complexes. Since it has been found that uranyl acetylacetonate monohydrate can exist in three different crystalline modifications,[9] this might explain the irregularities for solutions of this complex.

The irregularities in the solubility-temperature curves for uranyl oximate presumably have the same basis. The isolation and analysis of the solid oximate complex in equilibrium with one such solution, showed that it contained 34.57 per cent uranium as compared with 34.41 per cent uranium in the original material. This difference lies within the experimental uncertainty of the method. Thus, the indications are that a change in structure (but not in composition) of the solid phase in equilibrium with the solution could have occurred. From the solubility data it can also be determined that cobalt(III) acetylacetonate undergoes a phase change at 29°C.

---

[9] A. E. Comyns, *Chem. Rev.* **60**, 115 (1960).

In the discussion which follows, these irregular examples are provisionally ignored. It will be seen that this does not affect the general conclusions drawn from this work, as the theory is concerned primarily with orders of magnitude of the effects on solubilities.

One fundamental requirement that solutions must fulfill if they are to be considered as nearly regular is that the partial molal volume of the solute remain constant over the concentration range accessible to experimental investigation.[10] The partial molal volumes of cobalt(III) acetylacetonate and chromium(III) acetylacetonate computed from the data in Table 5 are found to be 169.81, $\sigma = 0.019$ and 181.48, $\sigma = 0.051$, respectively. The small value of the standard deviation for both of these values indicates that there are no unanticipated concentration dependent interactions in these solutions. Thus the behaviour of the volume changes when the concentrations of the solutions are varied is consistent with the behaviour of systems known to be regular. For the chromium(III) acetylacetonate the molal volume of the solid is 275.3 cm^3 while the partial molal volume in benzene is 181.48 cm^3, for the cobalt(III) acetylacetonate the corresponding values are 251.97 and 169.81 cm^3 respectively. For stannic iodide in benzene, which corresponds closely to the regular solution criteria in many respects, the corresponding values are 140.4 and 154.6 cm^3.[9] This indicates that the packing of the molecules in the solid complex leaves large holes. The melting points of these compounds are quite high so no estimate was made of the density of the supercooled liquid complexes.

For a regular solution one would expect the following relation to be valid

$$RT \ln (a_2/x_2) = v_2\phi_1^2 (\delta_1 - \delta_2)^2$$

where R is the gas constant, T is the absolute temperature, a_2 is the activity of the pure supercooled liquid solute, x_2 is the mole fraction of the solute in the solution, v_2 is the molal volume of the solute, ϕ_1 is the volume fraction of the solvent in the solution, and δ_1 and δ_2 are the solubility parameters of the solvent and the solute respectively. The use of this equation with solid solutes is attended by some difficulties which must be circumvented by approximations. Thus v_2 is, strictly speaking, the molal volume of the pure supercooled liquid solute at the temperature T. This parameter is usually not available for inner complex salts and there is no really satisfactory method of estimating it in these cases. We have used the molal volume of the solid complex for this term. In a similar manner, a_2 is usually not available. It has been suggested[11] that a_2 is approximately unity and this was used in our previous work. In the present paper a method is proposed for circumventing this assumption, so that it is not used. According to the regular solution theory, a_2 is also equal to the ideal solubility, x_2'.

The solubility data have been treated by simply assuming that they were described by the equation for a regular solution, and examining the results for consistency. Neither a_2 nor δ_2 is known for the solutions so that they both must be evaluated. This has been done by simple algebraic methods using the known values of v_2, ϕ_1 and x_2 for two or more solutions in solvents of known δ_1 values.

---

[10] E. B. SMITH and J. WALKEY, *Trans. Faraday Soc.* **56**, 1276 (1960).

[11] D. L. LEUSSING, *Treatise on Analytical Chemistry* (Edited by I. M. KOLTHOFF and P. J. ELVING), Part I, Vol. 1, pp. 681–4. Interscience, New York (1959).

The equation used was

$$\delta_2 = \frac{\delta_{1a} + \delta_{1b}}{2} - \frac{686.5}{v_2(\delta_{1a} - \delta_{1b})} (\log x_{2b} - \log x_{2a})$$

Here δ_{1a} and δ_{1b} are the solubility parameters of the solvents *a* and *b* and x_{2b} and x_{2a} are the solubilities of the solute (2) in these solvents at 25°C. This equation is based upon the fact that a_2, the activity of the pure supercooled liquid solute, is a constant at a given temperature.

Very satisfactorily constant δ_2 values were obtained for the three solutes studied, 12.2, $\sigma = 1.3$, 11.3, $\sigma = 1.7$, and 8.7, $\sigma = 1.1$ for the chromium(III) acetylacetonate, the uranyl acetylacetonate monohydrate, and the uranyl oxinate with an extra molecule of oxine, respectively, the data for which is presented in Table 6. When the large difference between the molal volume of the solute and the solvent in these systems is considered, the degree of regularity which is exhibited is gratifying. The δ_2 values which have been obtained by this method are much more realistic estimates than the provisional values reported earlier. This is due chiefly to the elimination of the assumption that $a_2 = 1$, which is a very poor one in the case of most inner complex salts with melting points considerably above 100° and occasionally above 200°C. From the data in Table 6 it can be computed that for the chloroform–toluene solvent pair system the values of a_2 for the three salts are 0.11, 1.4×10^{-3} and 3.2×10^{-4} respectively. It should be recalled that a_2 is the activity of the pure supercooled liquid solute and is less than the activity of the pure solid by an amount which increases as the temperature is decreased below the melting point. For iodine (m.p. 113.7°) at room temperature $a_2 = 0.258$, while for stannic iodide (m.p. 144.5°) a_2 is 0.146 (2,3)

TABLE 6. SOLUBILITY PARAMETERS OF SOME INNER COMPLEX SALTS

Solvent Pair	$Cr(C_5H_7O_2)_3$	$UO_2(C_5H_7O_2)_2 \cdot H_2O$	$UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$
	δ_2	δ_2	δ_2
CCl_4–nC_7H_{16}	12.4	8.6	8.3
p-$C_6H_4(CH_3)_2$–nC_7H_{16}	11.5	10.3	8.4
C_6H_{12}–$C_6H_5CH_3$	14.5	12.3	8.8
C_6H_{12}–$CHCl_3$	13.2	11.9	9.5
C_6H_6–CCl_4	10.6	13.9	7.8
C_6H_6–p-$C_6H_4(CH_3)_2$	12.5	10.6	7.4
$C_6H_5CH_3$–$CHCl_3$	11.0	11.2	10.7
Average	12.2	11.3	8.7
σ	1.3	1.7	1.1

The thermodynamic changes for the solution processes are presented in Table 7. These values are quite comparable with the values obtained for non-polar organic compounds of similar melting points.(12)

The reasonable constancy of the δ_2 values obtained for the inner complex salts

---

International Critical Tables, Vol. 5, p. 154 (1929).

TABLE 7 – STANDARD THERMODYNAMIC CHANGES FOR SOLUTION PROCESS

Complex	Solvent	$\Delta F\ \left(\frac{\text{kcal}}{\text{mole}}\right)^*$	$\Delta H\ \left(\frac{\text{kcal}}{\text{mole}}\right)$	$\Delta S\ \left(\frac{\text{cal}}{\text{deg-mole}}\right)$
$Cr(C_5H_7O_2)_3$	C_6H_6	1.555	2.128	1.93
	CCl_4	2.127	4.160	6.82
	$CHCl_3$	2.087	7.435	17.95
	C_6H_{12}	4.814	8.832	13.48
	p-$C_6H_4(CH_3)_2$	2.437	4.762	7.82
	$C_6H_5CH_3$	5.056	15.640	35.51
$UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$	C_6H_6	6.512	16.815	34.57
	CCl_4	6.006	10.059	13.60
	$CHCl_3$	5.567	9.980	14.80
	C_6H_{12}	6.278	10.860	15.37
	p-$C_6H_4(CH_3)_2$	5.961	14.220	27.72
	$C_6H_5CH_3$	6.099	4.794	4.34
	n-C_7H_{16}	6.334	12.480	20.54
$UO_2(C_5H_7O_2)_2 \cdot H_2O$	C_6H_6	4.268	3.434	2.79
	CCl_4	5.800	14.626	29.60
	$CHCl_3$	4.256	14.356	33.89
	C_6H_{12}	6.065	7.992	6.47
	p-$C_6H_4(CH_3)_2$	4.651	6.311	5.57
	$C_6H_5CH_3$	4.685	8.889	14.11
	n-C_7H_{16}	6.116	11.258	18.41
$Co(C_5H_7O_2)_3$	C_6H_6	2.041	1.754	1.00

* ΔF, ΔH and ΔS for $Cr(C_5H_7O_2)_3$ in benzene, carbon tetrachloride and chloroform were obtained from the first paper in this series.

indicates that predictions of the general solubility behavior of such materials should be possible from a very limited number of measurements. Once the characteristic values for a_2 and δ_2 have been obtained these will be useful for two purposes. The selection of good (or poor) solvents since these will have δ values close to (or far from) that of the complex, and calculation of approximate solubilities.

The magnitude of the δ_2 values obtained for these complexes indicates that they exert fairly large intermolecular forces in comparison with the hydrocarbons. A tentative explanation for this would seem to lie in the presence of large dipoles in these molecules. These would have a considerable effect on neighbouring solvent species even for molecules such as chromium(III) acetylacetonate where the dipoles are so disposed that the molecule as a whole has no net electric moment.

The solubility parameters of organic compounds can be predicted with reasonable accuracy by the use of the molal attraction coefficients given by SMALL.(13) While the amount of data presently available does not permit a ready extension of this method, it is possible to estimate the contribution of the octahedral chromium(III) to the solubility parameter of an inner complex salt by using the data on chromium(III) acetylacetonate.

Following SMALL, we may write

$$\delta = (\Sigma G)\frac{\rho}{M}$$

where ΣG is the summation of the additive contributions of the groups present in the molecule, ρ is the density of the compound, and M is its molecular weight. For $Cr(C_5H_7O_2)_3$, ΣG is

---

(13) P. S. SMALL, *J. Applied Chem.* 3, 75 (1953).

6	CH_3	1284
3	$-CH=$	333
3	$-C=O$	825
3	6-membered rings	300
3	etheral "O"	210
3	$C-$	57
3	conjugated systems	60
1	octahedral Cr(III)	X
	Total	$3069+X$

$$\delta = (3069 + X)\frac{1.266}{353.21} = 11.5$$

From this, X is 140. In a similar manner other group contributions due to various coordination centers may be evaluated once a suitable δ is obtained. The group contributions for a central species would be expected to be reasonably constant only so long as it preserves a given coordination number in *inner* complex salts. This method, does however, open the possibility of predicting the solubilities of inner complex salts from structural information only.

Acknowledgement—This work was supported in part by a grant from the U.S. Atomic Energy Commission for which we wish to express our gratitude.

J Inorg Nucl Chem 1963, Vol 25 pp 377 to 385 Pergamon Press Ltd Printed in Northern Ireland

ZUR FRAGE DER BINDUNGSVERHÄLTNISSE IN KOMPLEXVERBINDUNGEN DES EISEN(II) MIT 1,10-PHENANTHROLIN

K MADEJA
Institut fur anorganische Chemie der Universitat Greifswald
und
F KONIG*
Institut fur physikalische Chemie der Universitat, Frankfurt am Main

(*Received* 21 *July* 1962)

Zusammenfassung Es wird uber Messungen von magnetischen Suszeptibilitaten und von Reflexionsspektren an der Verbindungsreihe [$Fe^{II}phen_2X_2$] berichtet In Abhangigkeit vom Liganden X konnen dabei paramagnetische Verbindungen, deren Moment vier ungepaarten Elektronen entspricht oder diamagnetische Verbindungen erhalten werden Ihr spektrales Verhalten sowie die Lage des Quintett-Singulett Uberschneidungspunktes sind in Ubereinstimmung mit Vorstellungen der Ligandenfeldtheorie

Abstract Results of measurements of magnetic susceptibilities and reflexion spectra of the series of compounds [$Fe^{II}phen_2X_2$] are presented Depending on the ligand X it is possible to obtain paramagnetic compounds with an effective magnetic moment equal to four unpaired electrons or diamagnetic compounds The spectral behaviour and the position of the quintet-singlet crossover point are in accord with expectations of ligand field theory

KOMPLEXVERBINDUNGEN des zweiwertigen Eisens mit 1,10-Phenanthrolin sind vom bindungstheoretischen Standpunkt von besonderem Interesse Wahrend das [$Fe^{II}phen_3]^{2+}$-Ion diamagnetisch[1] ist, kann erwartet werden, dass bei Ersatz eines Phenanthrolin-moleküls im Eisen(II)-Komplex durch zwei einzahlige Liganden X innerhalb der Reihe [$Fe^{II}phen_2X_2$] sowohl diamagnetische Komplexe als auch solche vorkommen, deren magnetisches Moment 4 ungepaarten Elektronen entspricht Dies wird dann geschehen, wenn bei abnehmender Starke des Ligandenfeldes eine kritische Feldstarke erreicht wird, bei der anstelle des Singulett-Terms ein Quintett-Term zum Grundterm[2] wird Damit muss sich zugleich auch das spektrale Verhalten grundlegend andern

Gemass den Erwartungen zeigt das von SCHILT[3] hergestellte [$Fe^{II}phen_2(CN)_2$] Diamagnetismus, wahrend BASOLO und DWYER[4] fur das [$Fe^{II}phen_2Cl_2$] einen Paramagnetismus entsprechend 4 ungepaarten Elektronen fanden Im Gegensatz dazu steht eine altere Beobachtung von KLEMM, *et al*[5], wonach [$Fe^{II}phen_2J_2$] und [$Fe^{II}phen_2Br_2$] diamagnetisch sein sollen

Zur Klarung der Verhaltnisse wurden daher sowohl die bekannten Verbindungen der Zusammensetzung [$Fe^{II}phen_2X_2$] als auch einige neue Komplexe mit X Br^-, Cl , SCN , N_3 , OCN , HCOO und CN dargestellt und ihre magnetischen Momente sowie ihre Reflexionsspektren vermessen

---

* z Zt visiting fellow Mellon Institute Pittsburgh 13 Pennsylvania, U S A

[1] F H BURSTALL und R S NYHOLM *J Chem Soc* 3570 (1952)

[2] Y TANABE und S SUGANO, *J Phys Soc (Japan)* **9**, 753 766 (1954)

[3] A A SCHILT, *J Amer Chem Soc* **82**, 3000 (1960)

[4] F BASOLO und F P DWYER, *J Amer Chem Soc* **76**, 1454 (1954)

[5] W KLEMM, H JACOBI und W TILK, *Z Anorg Chem* **201**, 1 (1931)

EXPERIMENTELLER TEIL

Präparatives

Zur Darstellung der Verbindungen [Fe^{II}phen$_2$X$_2$] mit X = Br$^-$, Cl$^-$, SCN$^-$, N$_3^-$, OCN$^-$, HCOO$^-$ wurden die entsprechenden Eisen(II)-Pyridin-Komplexe der allgemeinen Zusammensetzung [Fe^{II}py$_n$X$_2$] oder auch die ihnen zugrunde liegenden wasserfreien Eisen(II)-Salze unter Luftausschluss (um Oxydation der Fe(II)-Salze zu vermeiden) in siedendem, wasserfreien Pyridin gelöst und die berechnete Menge wasserfreies 1,10-Phenanthrolin—gelöst in Pyridin—zugetropft. Dabei schieden sich die Bis-phenanthrolin-eisen(II)-komplexe als violette bis blaue Kristalle ab, die sich durch Extraktion mit Pyridin umkristallisieren liessen.

Die Verbindungen sind an trockener Luft beständig, disproportionieren aber in Gegenwart von Wasser, Alkohol oder Luftfeuchtigkeit unter Bildung des Tris-phenanthrolin-eisen(II)-komplexes. Über ihre Darstellung wird an anderer Stelle ausführlicher berichtet.[6]

Eine Verbindung [Fe^{II}phen$_2$I$_2$] liess sich weder auf diese Weise noch durch Abspalten von 1,10-Phenanthrolin durch Erhitzen von [Fe^{II}phen$_3$]I$_2$ im Vakuum über P$_2$O$_5$ auf 196 °C gewinnen.

[Fe^{II}phen$_2$(CN)$_2$] wurde nach SCHILT[3] durch Versetzen einer Lösung von [Fe^{II}phen$_3$]SO$_4$ mit KCN-Lösung hergestellt. Nach Extraktion des dunkelvioletten Niederschlages mit Alkohol in einer Soxhlet-Apparatur kristallisierte die Verbindung wasserfrei.

Zur Darstellung von [Fe^{II}phen$_3$]Cl$_2$ · 7H$_2$O wurde 1,10-Phenanthrolin-Hydrat und FeCl$_2$ · 4H$_2$O in Methanol gelöst, filtriert und der Tris-phenanthrolin-eisen(II)-komplex mit Aceton ausgefällt. Durch Umkristallisieren aus wenig Wasser erhält man das Heptahydrat.

Magnetische Messungen

Die Ermittlung der magnetischen Suszeptibilitäten der festen Proben erfolgte mittels einer Pendelwaage mit elektrischer Kompensation.[7]*

Die erhaltenen Werte der molaren Suszeptibilität χ_{mol} bei Zimmertemperatur (T = 289 K) finden sich in der zweiten Spalte der Tab. 1. Die um den diamagnetischen Anteil korrigierten molaren Suszeptibilitäten χ'_{mol} ergeben die effektiven magnetischen Momente $\mu_{eff} = 2.84\sqrt{(\chi'_{mol} \cdot T)}$. Die entsprechenden Werte von μ_{eff} gemessen in Einheiten des BOHRschen Magnetons sind in Spalte 4 der Tab. 1 enthalten.

Als diamagnetische Korrekturen wurden die folgenden Werte benutzt: 1,10-Phenanthrolin $-128 \cdot 10^{-6}$, Fe^{2+} $-13 \cdot 10^{-6}$, Br$^-$ $-35 \cdot 10^{-6}$, Cl$^-$ $-26 \cdot 10^{-6}$, SCN$^-$ $-31 \cdot 10^{-6}$, N$_3^-$ $-13 \cdot 10^{-6}$, OCN$^-$ $-21 \cdot 10^{-6}$, HCOO$^-$ $-16 \cdot 10^{-6}$, CN$^-$ $-13 \cdot 10^{-6}$.

TABELLE 1. MAGNETISCHE SUSZEPTIBILITÄTEN UND WERTE DES EFFEKTIVEN MAGNETISCHEN MOMENTES FÜR VERBINDUNGEN DER REIHE [Fe^{II}phen$_2$X$_2$]

χ_{mol} bedeutet die molare Suszeptibilität bei Zimmertemperatur (T = 289 K), μ_{eff} den nach Korrektur um den diamagnetischen Anteil sich ergebenden Wert des effektiven magnetischen Momentes in Einheiten des BOHRschen Magnetons

Verbindung	$\chi_{mol} \cdot 10^{6}$	diamagn. Korr. $\cdot 10^{6}$	μ_{eff} [B.M.]	μ_{eff} [B.M.] nach anderen Autoren
[Fe^{II}phen$_2$Br$_2$]	10 900	339	5.1_0	~ 0[illegible]
[Fe^{II}phen$_2$Cl$_2$]	11,050	315	5.1_2	$5.3^{(4)}$
[Fe^{II}phen$_2$(SCN)$_2$]	11 600	308	5.2_1	
[Fe^{II}phen$_2$(N$_3$)$_2$]	11,700	295	5.2_8	
[Fe^{II}phen$_2$(OCN)$_2$]	12 750	311	5.5_1	
[Fe^{II}phen$_2$(HCOO)$_2$]	13 055	300	5.5_6	
[Fe^{II}phen$_2$(CN)$_2$]	810	295	≈ 0	$0.68^{(3)}$

Absorptionsspektren

Absorptionsspektren des [Fe^{II}phen$_3$]$^{2+}$-Ions in Wasser wurden mit einem registrierenden Spektralphotometer Beckmann DK-2 unter Verwendung von Quarzkuvetten mit Schliffstopfen der Schichtlängen 4, 1 und 0.1 cm aufgenommen. Die Konzentrationen der Lösungen lagen zwischen 10^{-2} Mol/l und 10^{-4} Mol/l. Das erhaltene Absorptionsspektrum zeigt Abb. 1.

---

* Für die Durchführung der magnetischen Messungen sind wir Herrn Dr. R. PERTHEL vom Institut für magnetische Werkstoffe der Deutschen Akademie der Wissenschaften in Jena zu besonderem Dank verpflichtet.

(6) K. MADEJA, S. SCHMIDT und W. WILKE, In Vorbereitung.

(7) R. PERTHEL, *Z. Phys. Chem.* (Leipzig) **211**, 74 (1959).

Reflexionsspektren

Um bei der Aufnahme der Reflexionsspektren von Verbindungen der Reihe [Fe^{II}phen$_2$X$_2$] Disproportionierung durch Luftfeuchtigkeit auszuschliessen wurden einige besondere Vorkehrungen getroffen

Die Handhabung und Vorbereitung der Proben erfolgte in einer von trockenem hochgereinigten Stickstoff durchströmten glove-box Die zur Aufnahme der Reflexionsspektren benutzten Probenteller wurden in der glove-box mit den betreffenden Substanzproben beschickt und durch Auflegen einer mit Silikonfett abgedichteten plan-parallelen Platte aus optischem Quarzglas gegen Eindringen von Luft gesichert

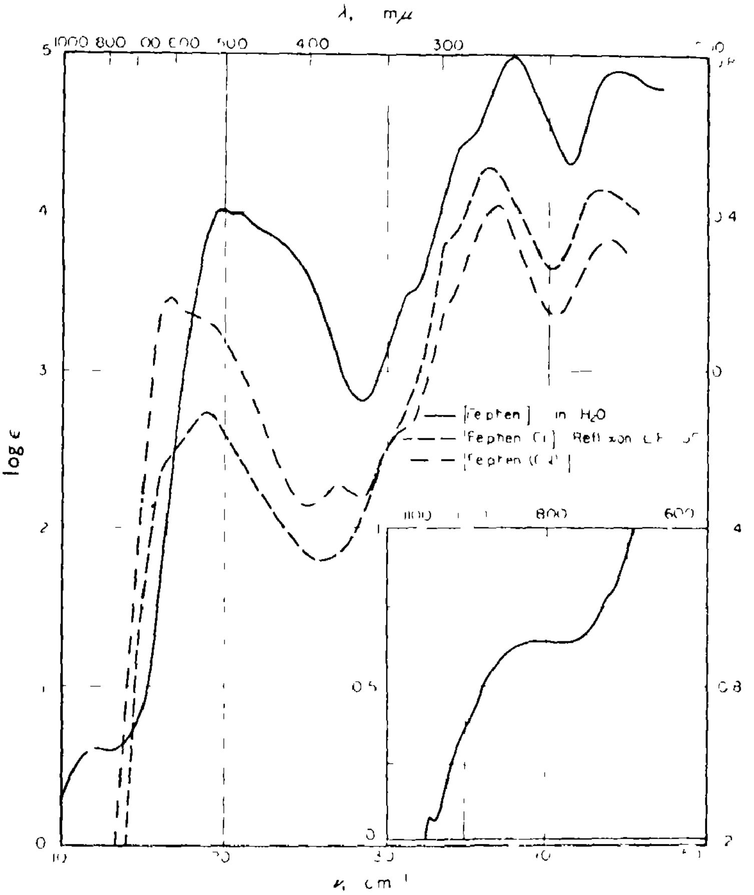


Abb 1 Absorptionsspektrum des Komplexions [Fe^{II}phen$_3$]$^{2+}$ in H$_2$O (c = 10^{-2} bis 10^{-4} [Mol/l], Schichtdicke 0 1 bis 4 [cm]), Reflexionsspektren von [Fe^{II}phen$_2$Cl$_2$] und [Fe^{II}phen$_2$(CN)$_2$] (LiF 1 50 verdünnt, Standard LiF)

Die Messung der so vorbereiteten Proben konnte in üblicher Weise am Spektralphotometer PMQ II der Fa Zeiss mit Remissionsansatz RA 2 vorgenommen werden Im Bereich von 220 bis 650 mμ diente ein SEV 1P28, im Bereich von 650 bis 1400 mμ eine Zelle spezieller Konstruktion* als Empfänger Die Korngrösse der Substanzen lag unterhalb von 5μ Im langwelligen Bereich wurden die Substanzen unverdünnt gemessen im Sichtbaren und UV wurden sie wegen der hohen Eigenabsorption mit Lithiumfluorid im Verhältnis 1 50 verdünnt Als Vergleichsstandard diente Lithiumfluorid Die Auswertung der Messdaten erfolgte nach der Methode von KORTUM(8) Die im folgenden angegebenen Reflexionsspektren (vgl Abb 1 und 2) enthalten den Logarithmus der KUBELKA-MUNK-Funktion log $f(R)$ in Abhängigkeit von der Wellenzahl $\bar{\nu}$ aufgetragen

---

* Der Entwicklungsabteilung der Fa Carl Zeiss, Oberkochen danken wir für die Überlassung eines im langwelligen und ultraroten Spektralbereich empfindlichen Empfängers

[8] G KORTUM und G SCHREYER, *Z Naturforsch* **11 A**, 74 (1956)

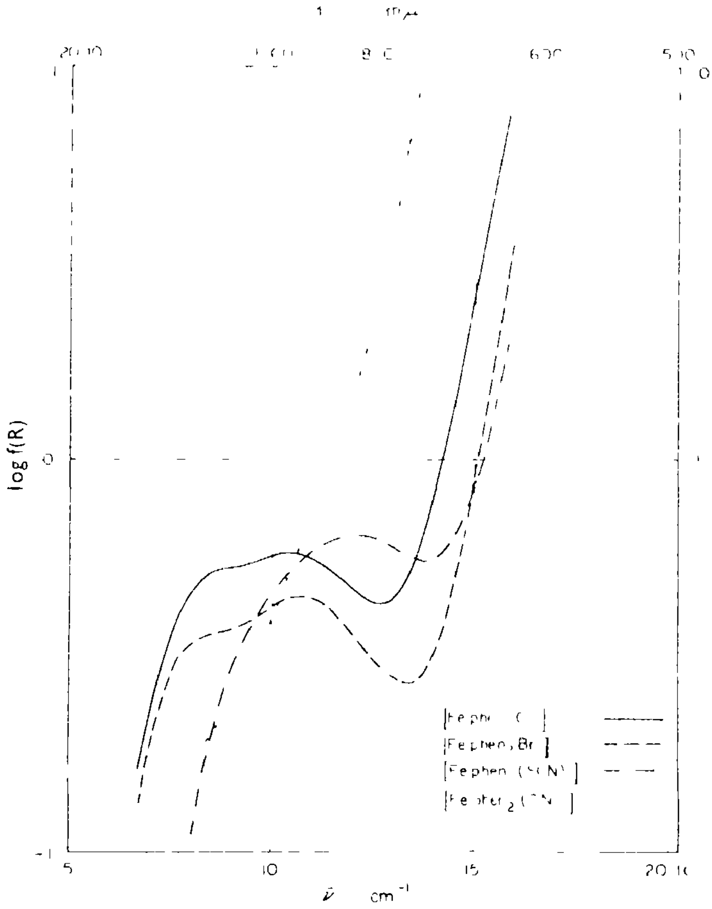


ABB. 2. – Langwelliger Teil der Reflexionsspektren von [Fe^{II}phen$_2$X$_2$] mit X = Cl, Br, SCN, CN. Rechte Ordinatenteilung für [Fe^{II}phen$_2$(CN)$_2$], linke Ordinatenteilung für alle übrigen Verbindungen.

DISKUSSION DER ERGEBNISSE

Magnetische Eigenschaften

Die von uns gemessenen Werte magnetischer Suszeptibilitäten von Verbindungen der Reihe [Fe^{II}phen$_2$X$_2$] sind in Tab. 1 angegeben. Von anderen Autoren fand einerseits SCHILT[3] für [Fe^{II}phen$_2$(CN)$_2$] ein μ_{eff} = 0.68 [B.M.], andererseits gaben BASOLO und DWYER[4] für [Fe^{II}phen$_2$Cl$_2$] ein μ_{eff} = 5.3 [B.M.] an, beides in Übereinstimmung mit den von uns ermittelten Momentwerten. Entgegen diesen Ergebnissen scheinen ältere Messungen von KLEMM, *et al.*[5] auf Diamagnetismus von [Fe^{II}phen$_2$Br$_2$] und [Fe^{II}phen$_2$J$_2$] hinzuweisen. Wir nehmen an, dass die beobachtete Diskrepanz in der schwierigen Präparation der Verbindungen ihre Ursache hat.

Oktaedrische Eisen(II)-Komplexe besitzen je nach Grösse der Kristallfeldaufspaltung entweder bei einem Grundzustand $^5T_{2g}(d\varepsilon^4 d\gamma^2)$ ein magnetisches Moment, das vier ungepaarten Elektronen entspricht, oder sie können diamagnetisch sein und haben dann den Grundzustand $^1A_{1g}(d\varepsilon^6)$. Ersetzt man sechs bzw. vier der einzähligen Liganden durch drei bzw. zwei zweizählige, so erfolgt infolge der damit verbundenen Symmetrieerniedrigung von O_h auf D_3 bzw. C_2 eine Aufspaltung des $^5T_{2g}$

TABELLE 2 — ABSORPTIONSSPEKTRUM VON $[Fe^{II}phen_3]^{2+}$
λ bedeutet die Wellenlänge, $\tilde{\nu}$ die Wellenzahl und ε den molaren dekadischen Extinktionskoeffizienten der Absorptionsmaxima. Eingeklammerte Werte der Wellenlänge wurden Schultern entnommen. CT bedeutet Elektronenübergangsbande (charge-transfer Bande)

Zuordnung	λ[mμ]	$\tilde{\nu}$[cm^{-1}]	ε
$^1A_{1g} \to {}^1T_{1g}$	1,115	8 960	1 2
$^1A_{1g} \to {}^3T_{2g}$	(1,050)	9,520	1 2
$^1A_{1g} \to {}^1T_{1g}$	815	12 260	4 4
$^1A_{1g} \to {}^1T_{2g}$	(680)	14,700	6 2
CT	510	19,600	10 600
CT	(488)	20,500	9 700
CT	(435)	23,000	7,200
^1L_b	(318)	31,400	3,150
^1L_a	(288)	34 700	27,600
^1B_b	265	37 700	95 000
^1C_b	225	44 500	81,000

TABELLE 3 — REFLEXIONSSPEKTREN VON KOMPLEXVERBINDUNGEN DER REIHE $[Fe^{II}phen_2X_2]$
λ bedeutet die Wellenlänge, $\tilde{\nu}$ die Wellenzahl der Bandenmaxima. Eingeklammerte Werte der Wellenlänge wurden Schultern entnommen. CT bedeutet Elektronenübergangsbande (charge-transfer Bande)

Verbindung	λ[mμ]	$\tilde{\nu}$[cm^{-1}]	Zuordnung
$[Fe^{II}phen_2Cl_2]$	1 180	8,470	$^5T_{2g} \to {}^5E_g$
	950	10 510	
	(600)	16 670	CT
	535	18,700	CT
	(325)	30 800	^1L_b
	(294)	34 000	^1L_a
	274	36,500	^1B_b
	230	43 500	^1C_b
$[Fe^{II}phen_2Br_2]$	1 180	8 470	$^5T_{2g} \to {}^5E_g$
	930	10 750	
	(590)	16 950	CT
	530	18 850	CT
	(325)	30 800	^1L_b
	(296)	33 800	^1L_a
	276	36 200	^1B_b
	230	43,500	^1C_b
$[Fe^{II}phen_2(SCN)_2]$	(1 020)	9 800	$^5T_{2g} \to {}^5E_g$
	830	12,050	
	(580)	17,230	CT
	530	18 860	CT
	(325)	30 800	^1L_b
	(296)	33 800	^1L_a
	272	36,800	^1B_b
	230	43 500	^1C_b
$[Fe^{II}phen_2(N_3)_2]$	(980)	10,200	$^5T_{2g} \to {}^5E_g$
	(820)	12 200	
	640	15 600	CT
	(590)	16 950	CT
	(540)	18 500	CT
	323	31 000	^1L_b

Tabelle 3 – (Cont'd)

Verbindung	λ[mμ]	$\bar{\nu}$[cm^{-1}]	Zuordnung
[Fe^{II}phen$_2$(N$_3$)$_2$] (Cont'd)	(295)	33 900	^1L_a
	272	36 800	^1B_b
	230	43 500	^1C_b
[Fe^{II}phen$_2$(OCN)$_2$]	(1 080)	9 250	$^5T_{2g} \to {}^5E_g$
	880	11 350	
	590	16 950	CT
	570	17 550	CT
	540	18 500	CT
	(325)	30 800	^1L_b
	(298)	33,550	^1L_a
	272	36 800	^1B_b
	230	43 500	^1C_b
[Fe^{II}phen$_2$(HCOO)$_2$]	(960)	10 400	$^5T_{2g} \to {}^5E_g$
	(800)?	12 500	
	595	16 800	CT
	(565)	17,700	CT
	540	18 500	CT
	(325)	30 800	^1L_b
	(298)	33 550	^1L_a
	272	36,800	^1B_b
	230	43 500	^1C_b
[Fe^{II}phen$_2$(CN)$_2$]	(800)?	12 500	$^1A_{1g} \to {}^1T_{1g}$
	600	16 670	CT
	(560)	17,850	CT
	(530)	18 850	CT
	370	27 000	CT ?
	(325)	30 800	^1L_b
	(296)	33 800	^1L_a
	274	36 500	^1B_b
	228	43 900	^1C_b

Grundzustandes gemäss

$$\underset{(O_h)}{T_{2g}} \to \underset{(D_3)}{E + A_1} \to \underset{(C_2)}{2A + B},$$

der $^1A_{1g}$ Zustand kann hingegen nicht weiter aufspalten. Bei oktaedrischen Eisen(II)-Komplexen vom high-spin Typ ist demnach ein dreifach bahnentarteter Zustand Grundzustand und damit ist ein Bahnmomentbeitrag zu erwarten. Demgegenüber wird mit zunehmender Beteiligung niedriger symmetrischer Feldkomponenten der Symmetrie D_3 bzw. C_2 die Bahnentartung aufgehoben, und damit sollte in erster Näherung auch der Bahnmomentbeitrag immer mehr unterdrückt werden.

Vergleichen wir mit den gemessenen Suszeptibilitätswerten (s. Tab. 1), so stellen wir fest: Das Komplexion [Fe^{II}phen$_3$]$^{2+}$ ist diamagnetisch(1)*. Von den hier beschriebenen Verbindungen der Reihe [Fe^{II}phen$_2$X$_2$] ist nur [Fe^{II}phen$_2$(CN)$_2$] diamagnetisch. Durchläuft demnach der Ligand X die spektrochemische Serie in Richtung abnehmender Stärke des Ligandenfeldes, so wird schliesslich ein Punkt erreicht, bei dem anstelle des Singulett-Terms ein Quintett-Term Grundterm wird. Diese kritische Feldstärke sollte – wie man auch aus dem Gang der individuellen Stabilitätskonstanten bei der Komplexbildung des [Fe^{II}(H$_2$O)$_6$]-Ions mit 1,10-Phenanthrolin vermuten kann $(k_1 > k_2 \quad k_3)$[9]—etwa in dem Bereich zwischen den Komplexionen $[Fe^{II}phen_3]^{2+}$ und $[Fe^{II}phen_2(H_2O)_2]^{2+}$ erreicht werden. Da es bis jetzt nicht gelungen ist, Komplexionen wie $[Fe^{II}phen_2(NH_3)_2]^{2+}$ oder $[Fe^{II}phen_2(H_2O)_2]^{2+}$ herzustellen, bei denen der Ligand X ein etwa in der Mitte der spektrochemischen Serie gelegener Dipolligand ist, kann zunächst über die Lage des Überschneidungspunktes in der Verbindungsreihe $[Fe^{II}phen_2X_2]$ noch keine genauere Aussage gemacht werden.

---

* Eigene Messungen

Bei Gültigkeit der reinen Spinformel $\mu_{eff} = \sqrt{\{4S(S+1)\}} = \sqrt{\{n(n+2)\}}$ [B.M.] sollte man bei 4 ungepaarten Elektronen ein effektives magnetisches Moment von 4.90 [B.M.] erwarten. Dabei bedeutet S die Spinquantenzahl und n die Anzahl ungepaarter Elektronen. Die von uns untersuchten paramagnetischen Komplexe $[Fe^{II}phen_2X_2]$ weisen alle etwas erhöhte Momentwerte auf. Die durch die Differenz gegebenen Werte der Bahnmomentbeiträge liegen zwischen 0.20 und 0.66 [B.M.]. Werden Verzerrungen der Symmetrie in Richtung $O_h \rightarrow C_2$ als einzige Ursache für die abnehmende Grösse der Bahnmomentbeiträge angesehen, so ist in der Reihe X $HCOO$, OCN, N_3, SCN, Cl, Br mit zunehmender Abweichung des Ligandenfeldes von streng oktaedrischer Symmetrie zu rechnen.*

Spektroskopische Eigenschaften

Für die Art der zur Beobachtung gelangenden $d \quad d$ Übergänge ist es wesentlich, ob die betreffende Verbindung $[Fe^{II}phen_2X_2]$ zum paramagnetischen oder zum diamagnetischen Typ gehört. Bezeichnet man im oktaedrischen Fall die Grösse der T_{2g} E_g Separation Δ am Überschneidungspunkt von $^5T_{2g}$ und $^1A_{1g}$ mit Π, so werden oktaedrische Eisen(II)-Komplexe für $\Delta \quad \Pi$ ein Moment von vier ungepaarten Elektronen aufweisen, für $\Delta \quad \Pi$ jedoch diamagnetisch sein. Die Spinpaarungsenergie Π ergibt sich[10, 11] für die Konfiguration d^6 zu

$$\Pi \quad 2\tfrac{1}{2}B \quad 4C \quad 1076 \quad 9\alpha$$

Dabei ist die Konfigurationswechselwirkung mit höheren Zuständen gleicher Rasse durch Anwendung der Störungstheorie zweiter Ordnung[12] näherungsweise mitberücksichtigt worden, ferner wurde die Korrektur nach TREES[13] einbezogen. B und C bedeuten die RACAH-Parameter des Zentralions im Komplex, α ist die Konstante der TREESschen Korrektur.

Die Absorptionsspektren diamagnetischer Eisen(II)-Komplexe sollten neben intensitätsschwachen Interkombinationsübergängen im wesentlichen zwei Banden aufweisen, die von den beiden Übergängen $^1A_{1g} \rightarrow {}^1T_{1g}$ und $^1A_{1g} \rightarrow {}^1T_{2g}$ herrühren. Ihre Anregungsenergien betragen bei alleiniger Berücksichtigung der Diagonalelemente in den zugehörigen Säkularproblemen[2] $\Delta \quad C$ und $\Delta \quad 16B \quad C$. Bei Mitberücksichtigung der Konfigurationswechselwirkung und der Korrektur nach TREES mit dem für das freie Ion Fe^{2+} gültigen Wert von $\alpha \quad 67\ cm^{-1}$ erhält man für das

---

* Eine andere Möglichkeit zur Erklärung der Abnahme der Bahnmomentbeiträge ist zunehmende Kovalenz der Bindung zwischen Zentralion und Ligand X. Diese Annahme kann dadurch gestützt werden, dass die obige Reihenfolge abnehmender Grösse der Bahnmomentbeiträge zugleich annähernd der nephelauxetischen Reihe folgt.

[9] H. M. N. H. IRVING, *International Conference on Co-ordination Chemistry* p. 16. London (1959).

[10] J. S. GRIFFITH, *The Theory of Transition-Metal Ions*. Cambridge Univ. Press (1961).

[11] E. KÖNIG und H. L. SCHLÄFER, *Z. Phys. Chem. N.F.* **34**, 355 (1962).

[12] C. K. JØRGENSEN, *Energy Levels of Complexes and Gaseous Ions*. Gjellerups Forlag. København (1957).

[13] R. E. TREES, *Phys. Rev.* **83**, 756 (1951).

Komplexion $[Fe^{II}phen_3]^{2+}$ die Anregungsenergien

$$\Delta E(^1A_{1g} \rightarrow {}^1T_{1g}) = \Delta - C + 1321 + 536$$

$$\Delta E(^1A_{1g} \rightarrow {}^1T_{2g}) = \Delta + 16B - C + 4803 - 536$$

Im Absorptionsspektrum des Komplexions $[Fe^{II}phen_3]^{2+}$ beobachtet man* bei 12 260 cm⁻¹ eine Bande, die auf Grund ihrer Intensitat dem Ubergang $^1A_{1g} \rightarrow {}^1T_{1g}$ zugeordnet werden muss (vgl. Abb. 1). Der Ubergang $^1A_{1g} \rightarrow {}^1T_{2g}$ wird grosstenteils von der folgenden hohen Bande uberdeckt und macht sich nur in einer leichten Inflexion bemerkbar†. Seine Lage kann durch Zerlegung in GAUSS-Kurven zu 14 700 cm⁻¹ ermittelt werden (11). Da keine Bandenaufspaltungen zu erkennen sind, darf man $[Fe^{II}phen_3]^{2+}$ in erster Naherung als oktaedrisch ansehen. Dann erhalt man aus den Anregungsenergien der beiden *d-d* Ubergange $B = 602$ cm⁻¹ und $\Delta = 13\,110$ cm⁻¹‡.

Setzt man $C = 4.5B$ und ermittelt man mit dem obigen Wert von B und $\gamma = 67$ cm⁻¹ die Spinpaarungsenergie Π, so erhalt man $\Pi = 11\,900$ cm⁻¹. Paramagnetische Eisen(II)-Komplexe oktaedrischer Symmetrie besitzen ausser Interkombinationsbanden nur eine meist unter der Wirkung des JAHN-TELLER-Effektes verbreiterte Bande, die dem Ubergang $^5T_{2g} \rightarrow {}^5E_g$ entspricht. Fur das Ion $[Fe^{II}(H_2O)_6]^{2+}$ betragt ihre Anregungsenergie(12) $\Delta = 10.400$ cm⁻¹. Da andererseits fur $[Fe^{II}phen_3]^{2+}$ ein $\Delta = 13\,110$ cm⁻¹ erhalten worden ist, sollte der Uberschneidungspunkt der beiden Terme $^5T_{2g}$ und $^1A_1$, bei einer Feldstarke liegen, die etwa in der Mitte zwischen den Liganden H_2O und phen anzunehmen ist. Dazu kann als weitere Stutze dienen, dass dem Ion $[Fe\,en_3]^{2+}$ auf Grund seines Absorptionsspektrums(18) mit $\Delta = 11\,400$ cm⁻¹ ein paramagnetischer Grundzustand $^5T_{2g}$ zukommt.

Bei Komplexverbindungen $[Fe^{II}phen_2X_2]$ kann wegen der niedrigeren Symmetrie nicht mehr ein Wert fur Δ angegeben werden. Jedoch beobachtet man ebenso wie beim $[Fe^{II}(H_2O)_6]^{2+}$ bei den paramagnetischen Verbindungen dieser Reihe eine langwellige Bande, deren Unsymmetrie auf statische Feldkomponenten niedriger Symmetrie zuruckzufuhren sein durfte (vgl. Abb. 2). So weit die beiden Maxima sauber getrennt sind, zeigen sie eine Aufspaltung von ca. 2.000 cm⁻¹, die in der gleichen Grossenordnung liegt wie die JAHN-TELLER-Aufspaltung beim $[Fe^{II}(H_2O)_6]^{2+}$-Ion.

Diamagnetische Verbindungen der gleichen Reihe weisen nur eine langwellige Bande auf, die ebenso wie beim $[Fe^{II}phen_3]^{2+}$ dem im oktaedrischen Fall mit $^1A_{1g} \rightarrow {}^1T_{1g}$ bezeichneten Ubergang entspricht und sich mit wachsender Starke des

---

* Das Absorptionsspektrum des Ions $[Fe^{II}phen_3]^{2+}$ ist schon mehrfach Gegenstand von Untersuchungen gewesen(14, 15, 16), jedoch fehlten bisher genauere Angaben uber die Existenz langwelliger *d-d* Ubergange.

† Zur genaueren Darstellung des langwelligen Teils des Absorptionsspektrums von $[Fe^{II}phen_3]^{2+}$ und zur Diskussion der Interkombinationsubergange vgl. E. Konig und H. L. Schlaffer(11).

‡ Der erhaltene Wert fur B erscheint auch auf Grund der folgenden rohen Abschatzung plausibel. Der B-Wert des freien Ions

Co³⁺-Ions (d^6) nimmt im oktaedrischen Feld von Stickstoffliganden um 38 % von 1 100 auf 680 cm⁻¹ ab(10). Rechnet man fur das Fe²⁺-Ion mit einer gleich grossen Abnahme, so erhalt man ausgehend vom B-Wert des freien Ions von 940 cm⁻¹ einen Wert von 585 cm⁻¹ fur das Ion im Komplex.

(14) J. Csaczar, *Acta Chim. Hung.* **24**, 55 (1960).

(15) J. Csaczar und E. Horvath, *Acta Chim. Hung.* **24**, 259 (1960).

(16) C. K. Jørgensen, *Acta Chem. Scand.* **11**, 166 (1957).

(17) D. S. McClure in F. Seitz und D. Turnbull, *Solid State Physics*, Vol. 9. Academic Press, New York (1959).

(18) M. Ciampolini, P. Paoletti und L. Sacconi, *J. Chem. Soc.* 4553 (1960).

Ligandenfeldes nach kürzeren Wellen verschiebt. Beim $[\mathrm{Fe^{II}phen_2(CN)_2}]$ wird sie bereits fast völlig vom Anstieg der folgenden hohen Bande verdeckt. Dies gilt ebenso für den Übergang $^1A_{1g} \rightarrow {}^1T_{2g}$. Die unterschiedliche Erscheinungsform der langwelligen Absorptionsbanden in Reflexionsspektren der Reihe $[\mathrm{Fe^{II}phen_2X_2}]$ ermöglicht demnach eindeutige Aussagen über die Multiplizität des Grundzustandes der einzelnen Verbindungen und dient damit zur Stützung der Ergebnisse magnetischer Suszeptibilitätsmessungen.

An die Ligandenfeldbanden schliessen sich nach kurzen Wellen Banden hoher Intensität an ($\log \varepsilon \approx 4$), die im allgemeinen paritätserlaubten Übergängen zwischen $d\varepsilon$- und $d\gamma$-Zuständen am Zentralion und antibindenden π-Zuständen des heterocyclischen Liganden zugeordnet werden.(16) Dabei können meist zwei bis drei einzelne Maxima unterschieden werden (vgl. Tab. 2 und 3).

Die im UV bei ca. 36,500 und 43,500 $\mathrm{cm^{-1}}$ auftretenden intensiven Banden stellen die im wesentlichen unveränderten Übergänge zwischen π-Zuständen des 1,10-Phenanthrolins dar, die unter der Wirkung der Zentralionenladung geringfügig nach langen Wellen verschoben worden sind. Die beobachteten Bandenverschiebungen betragen für die erste der beiden obigen Banden 1,200–1,800 $\mathrm{cm^{-1}}$, für die zweite $\approx$ 600 $\mathrm{cm^{-1}}$, sie sind in Übereinstimmung mit den Ergebnissen quantenmechanischer Modellrechnungen.(19)

Da die Absorptionsspektren von N-Heterocyclen denen der entsprechenden aromatischen Kohlenwasserstoffe sehr ähnlich sind, konnte ZANKER(20) eine darauf beruhende Klassifizierung ihrer Banden vornehmen. Beim freien 1,10-Phenanthrolin erscheinen am langwelligen Abfall der bei 38 000 $\mathrm{cm^{-1}}$ gelegenen ersten hohen Absorptionsbande zwei weitere weniger intensive Banden mit einer fein ausgeprägten Schwingungsstruktur.(21) In Analogie zum Phenanthren(22) beobachtet man demnach im nahen UV insgesamt vier Banden, die man bei Zugrundelegung der PLATTschen Nomenklatur(23) in der Reihenfolge steigender Wellenzahlen mit ^1L_b, ^1L_a, ^1B_b und ^1C_b bezeichnen kann. Die ^1L_b-Bande besteht bereits bei Zimmertemperatur aus einer Serie von fünf Schwingungsteilbanden mit einer Wellenzahldifferenz von etwa 700 $\mathrm{cm^{-1}}$, die ihren Ausgang von dem bei 29,650 $\mathrm{cm^{-1}}$ gelegenen 0-0-Übergang nimmt.

Wie das Absorptionsspektrum des Komplexions $[\mathrm{Fe^{II}phen_3}]^{2+}$ und die Reflexionsspektren von Verbindungen der Reihe $[\mathrm{Fe^{II}phen_2X_2}]$ zeigen, wird die Schwingungsstruktur beim Einbau des 1,10-Phenanthrolins in einen Komplex verwischt, die beiden Banden ^1L_b und ^1L_a zeigen sich jedoch in zwei Schultern, die meist bei etwa 31,000 und 34,000 $\mathrm{cm^{-1}}$ auftreten (vgl. Tab. 2 und 3).

Anerkennungen. Die Autoren danken Herrn Prof. Dr. H. L. SCHLÄFER, Frankfurt am Main und Herrn Prof. Dr. S. HERZOG, Greifswald für ihr förderndes Interesse und für zahlreiche Diskussionen.

---

(19) H. L. SCHLÄFER, *Z. Phys. Chem. N.F.* **8**, 373 (1956).

(20) V. ZANKER und W. SCHMID, *Chem. Ber.* **90**, 2253 (1957).

(21) F. KÖNIG, unveröffentlichte Messungen.

(22) H. ZIMMERMANN und N. JOOP, *Z. Elektrochem.* **65**, 66 (1961).

(23) J. R. PLATT, *J. Chem. Phys.* **17**, 484 (1949).

J. Inorg. Nucl. Chem. 1963. Vol. 25, pp. 387 to 393. Pergamon Press Ltd. Printed in Northern Ireland

HALIDE COMPLEXES OF THE LANTHANIDE ELEMENTS

G. R. CHOPPIN and P. J. UNREIN*
Department of Chemistry, Florida State University, Tallahassee, Florida

(*Received* 27 *June* 1962, *in revised form* 16 *August* 1962)

Abstract—The stability constants for formation of $CeCl^{2+}$, $CeBr^{2+}$, $EuCl^{2+}$, $EuBr^{2+}$, EuI^{2+}, YCl^{2+}, and YBr^{2+} have been measured at an ionic strength of 1.0 M by a liquid cation exchanger extraction method. Constants for formation of $CeCl_2^{+}$, $EuCl_2^{+}$ and $EuBr_2^{+}$ are also reported. The enthalpy and entropy values indicate that these complexes are ionic and possibly of the outer sphere type.

RECENTLY WHITE *et al.*(1) used the liquid cation exchanger dinonyl naphthalene sulphonic acid to study the chloride complexes of Fe(III) and In(III) ions. The stability constants were in satisfactory agreement with values reported using other techniques. This seemed a promising system to use to measure the stability constants of chloride, bromide, and iodide complexes of representative lanthanide elements. Earlier studies of $LaCl^{2+}$,(2) $CeCl^{2+}$,(3) $CeBr^{2+}$, and CeI^{2+} (4) have indicated stability constants less than unity, but the error limits are rather large, and the values were not obtained at the same ionic strength. We have studied more systems at a constant ionic strength.

Also, the enthalpy and entropy of formation of $EuCl^{2+}$ were measured.

EXPERIMENTAL

Materials. ^{152,154}Eu, ^{144}Ce, ^{22}Na and ^{91}Y were obtained from the Oak Ridge National Laboratory as carrier-free isotopes. ^{170}Tm was prepared by neutron irradiation of Tm_2O_3 in the ETR at ORNL. The original chloride solutions were diluted with 0.1 M $HClO_4$ to bring the tracer activity to a convenient working level. In all cases the chloride ion concentration of these final stock solutions was less than 0.0005 M.

Dinonyl naphthalene sulphonic acid (referred to as HD) was supplied as a 38.2 per cent solution in n-heptane through the courtesy of the R. T. Vanderbilt Co., Inc. The stock solution was analyzed by the extraction of a known volume of the solution with standard NaOH, followed by titration of an aliquot of the aqueous phase with standard HCl. The HD was diluted with n-heptane for use.

All halide acids were reagent grade, diluted to volume, and standardized with standard NaOH. Standardizations were made by potentiometric titration to insure concentrations accurate to within one part per thousand. The reagent grade HI was passed through an anion exchange resin bed prior to dilution for immediate use. The aqueous and organic solutions were pre-equilibrated with each other prior to use.

Procedure. The procedure followed that by WHITE *et al.*(5) Mixing was continued for 4–24 hr although studies of the rate of equilibration showed that it was obtained in less than an hour. Better precision was attained in the distribution ratio by allowing the two phases to settle for a longer period of time, i.e., 12–24 hr.

The radionuclides which decay by γ-emission were counted directly as liquid aliquots using a NaI Scintillation counter. The nuclides which decay by β-emission were counted in a thin end-window

---

* Based on an M.S. thesis submitted to Florida State University, June, 1962, by P. J. U.

(1) J. M. WHITE, P. KELLY and N. C. LI *J. Inorg. Nucl. Chem.* **16**, 337 (1961).

(2) R. E. CONNICK and K. L. MATTERN, reported by CONNICK and MCVEY *J. Chem. Soc.* **75**, 474 (1953).

(3) R. E. CONNICK and S. W. MAYER *J. Amer. Chem. Soc.* **73**, 1176 (1951).

(4) S. W. MAYER and S. D. SCHWARTZ, *J. Amer. Chem. Soc.* **75**, 222 (1953).

(5) J. M. WHITE, P. TANG and N. C. LI, *J. Inorg. Nucl. Chem.* **14**, 255 (1960).

Geiger-Mueller counter. The samples were prepared in the following way. The aliquot from the organic phase was placed in a steel pan, evaporated to dryness, and ignited in the flame of a Fisher burner to insure that loss in count rate due to sample self-absorption was both minimized and standardized. The aliquot from the aqueous phase was placed in a glass planchet and evaporated to dryness under a heat lamp. Counting corrections had to be made because of the difference in the geometry and in the material of the counting planchets.

RESULTS

To determine the influence of hydrogen ion concentration and HD concentration on the distribution of a metal ion the distribution of europium(III) was studied by first varying the concentration of hydrogen ion in the aqueous phase and then varying the HD concentration in the organic phase. The hydrogen ion dependency was not studied at constant ionic strength but rather at different perchloric acid concentrations. As seen in Fig. 1 the extraction of europium(III) was found to have an inverse third power dependency upon the hydrogen ion concentration in the equilibrated aqueous phase. These results were also obtained by WHITE *et al.*[3] for the distribution of In(III) and Fe(III). For the distribution of the bivalent metal ions, cobalt (II), maganese(II), and zinc(II), they found an inverse second-power dependency on hydrogen ion concentration and direct first-power dependency on HD concentration. The dependency of Eu(III) extraction on HD concentration in the organic phase is shown in Fig. 2 to be first power. WHITE *et al.*, have interpreted such a dependency on HD concentration to reflect micelle formation in moist heptane.

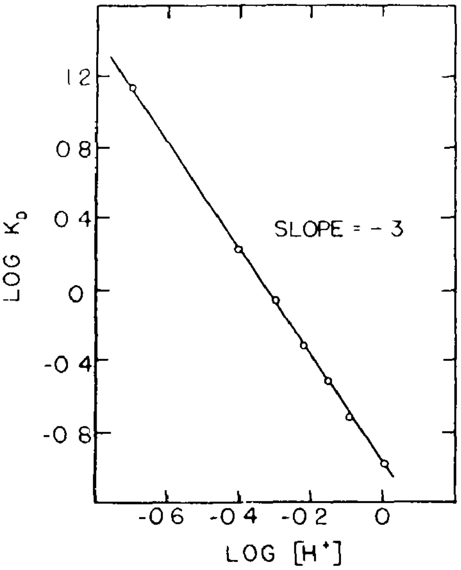


FIG. 1.—Dependency of Eu(III) extraction on [H⁺] at 25°C from $HClO_4$ aqueous phase into 0.0013 F HD organic phase.

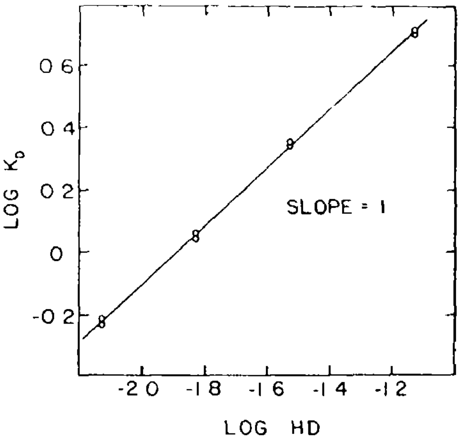


FIG. 2.—Dependency of Eu(III) extraction on [HD] at 25°C from 1.00 M $HClO_4$ aqueous phase into HD organic phase.

The extraction of the metal ion by HD is described by the following equation

$$\mathrm{M_A^{+3} + (HD)_{xO} \rightleftharpoons M(H_{x-3}D_x)_O + 3H_A^+}$$

where the subscripts A and O denote the aqueous and organic phases, respectively.

By defining the distribution ratio, K_d, as the concentration of the nuclide in the organic phase divided by the concentration of the nuclide in the aqueous phase, the above equation takes the form

$$K_d = \frac{[M(H_{x-1}D_x)_3]_o}{[M^{3+}]_A} = \frac{k[(HD)_x]_o^3}{[H^+]_A^3}$$

where k is the concentration equilibrium quotient. A typical set of data for an extraction experiment is given in Table 1.

TABLE 1 EXPERIMENT C DETERMINATION OF STABILITY CONSTANTS FOR Eu(III) COMPLEXES WITH CHLORIDE ION

Temperature 25.0 ± 0.2 C
Initial volume of both phases 2.0 ml
Volume of aliquots taken 0.5 ml
Tracer used Eu-152, 154
Counter used NaI (Tl) well scintillation counter initial concentrations
Organic HD 0.01 F
Aqueous (1) HCl 1.00 M $HClO_4$ 0
(2) HCl 0.94 M $HClO_4$ 0.06 M
(3) HCl 0.88 M $HClO_4$ 0.12 M
(4) HCl 0.80 M $HClO_4$ 0.20 M
(5) HCl 0.70 M $HClO_4$ 0.30 M
(6) HCl 0.60 M $HClO_4$ 0.40 M
(7) HCl 0.40 M $HClO_4$ 0.60 M
(8) HCl 0.20 M $HClO_4$ 0.80 M
(9) HCl 0 $HClO_4$ 1.00 M

Sample	Activity in organic phase (Counts/5 min)	Activity in aqueous phase (Counts/5 min)	K_d
1	12704	29135	0.436
2	13204	29025	0.455
3	13491	27987	0.482
4	14094	28093	0.501
5	14563	27473	0.530
6	15014	26549	0.566
7	15668	24658	0.635
8	12932	17435	0.742
9	18618	21560	0.864

When the concentration of $[H^+]$ and HD is kept constant, the stability constants for the lanthanide halide complexes can be calculated from measurements of the variation of K_d with change in concentration of the complexing halide ion.

The equation for this calculation is

$$\frac{K_d^0}{K_d} = 1 + k_1[A] + k_1k_2[A]^2 + \cdots$$

where $k_1, k_2, \ldots k_n$ are the step-wise stability constants for the formation of the complexes MA, …, MA_n and K_d^0 is the distribution ratio in the absence of complexing ligand. If only the first complex is formed, a plot of $1/K_d$ vs [A] gives a straight line whose slope is equal to k_1/K_d^0. If the second complex in the series is also formed, a plot of $[(K_d^0/K_d) - 1]/[A]$ vs [A] will give a straight line whose slope is equal to k_1k_2 and whose intercept is k_1. The data for Eu(III) and Cl^- are plotted

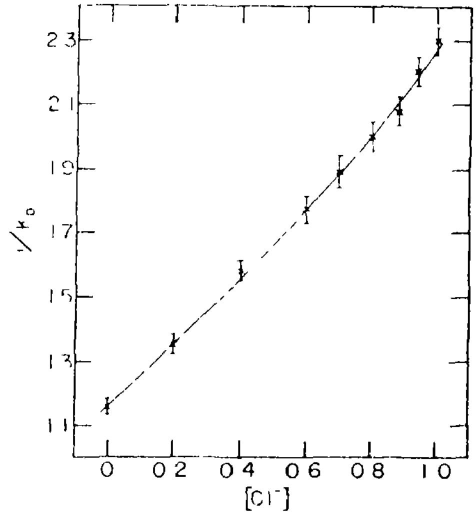


FIG. 3 Extraction of Eu(III) (Expt C) at 25 C as a function of [Cl⁻] with 1 00 M ionic strength in the aqueous phase and 0 01 F HD in the organic

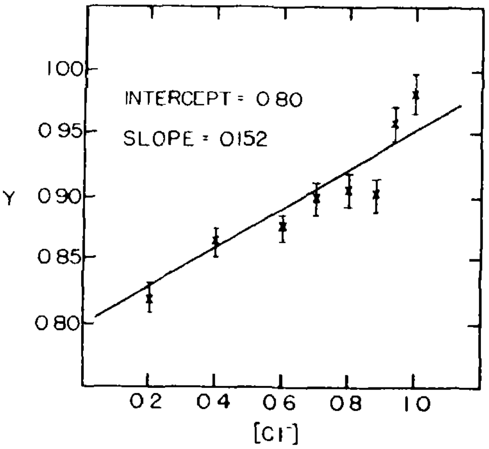


FIG. 4 Extraction of Eu(III) (Expt C) at 25 C as a function of [Cl⁻] where Y = [(K_d^0/K_d) − 1]/[A]]

in both ways in Figs 3 and 4 In the analysis of the data for the liquid extraction studies of the lanthanide halide complexes, no evidence for the formation of the MA_3 and higher order complexes was found This is not surprising since the halide complexes are weak and the concentration of the complexing anion never exceeds one molar

The stability constants determined for the lanthanide halides, MA^{2+} and MA_2^{+}, are listed in Table 2 These constants were obtained by a least squares analysis of the slope of [(K_d^0/K_d) − 1/[A]] vs [A]

TABLE 2 —STABILITY CONSTANTS FOR THE LANTHANIDE HALIDES AT 25 C

Trivalent metal ion	Complexing anion	Expt	Ionic strength	k_1	k_2
Ce	Cl	A	1 0	0 78 ± 0 14	0 33 ± 0 10
Ce	Cl	B	1 0	0 83 ± 0 12	0 20 ± 0 10
Eu	Cl	C	1 0	0 80 ± 0 12	0 19 ± 0 10
Eu	Cl	D	1 0	0 79 ± 0 11	0 30 ± 0 10
Eu	Cl	E	0 87	0 82 ± 0 12	0 19 ± 0 10
Eu	Br	F	1 0	0 58 ± 0 09	0 35 ± 0 20

In many of the experiments, the data were not sufficiently accurate to determine the value for both k_1 and k_2, due to the inherent error in K_d^0 To indicate the effect of neglecting MA_2 formation, the experiments of Table 2 have been recalculated for k_1 only from a least squares evaluation of the slope of $1/K_d$ vs [A] and are listed in Table 3 along with those where it was not feasible to calculate a k_2 value

DISCUSSION

For many of the lanthanide-halide systems, a plot of $1/K_d$ vs [A] departed from a linear relationship when the complexing anion exceeded a concentration of 0 6 M

TABLE 3 —STABILITY CONSTANTS FOR THE LANTHANIDE HALIDES AT 25°C

Trivalent metal ion	Complexing anion	Expt	Ionic strength	k_1
Ce	Br	G	1.0	0.63 ± 0.08
Ce	Br	H	1.0	0.67 ± 0.08
Eu	Cl	I	1.0	0.91 ± 0.11
Eu	Cl	J	1.0	0.88 ± 0.10
Eu	I	K	1.0	0.49 ± 0.06
Y	Cl	L	1.0	0.94 ± 0.11
Y	Cl	M	1.0	0.92 ± 0.11
Y	Br	N	1.0	0.71 ± 0.08
Tm	Cl	O	1.0	1.35 ± 0.16
Ce	Cl	A	1.0	0.88 ± 0.10
Ce	Cl	B	1.0	0.91 ± 0.11
Eu	Cl	C	1.0	0.89 ± 0.11
Eu	Cl	D	1.0	0.90 ± 0.11
Eu	Br	E	1.0	0.65 ± 0.08

(e.g., see Fig. 3). This departure from a linear relationship was assumed to be due to the formation of the second complex MA_2^+. However, evidence for a k_2 stability constant had not been reported by WHITE et al.[1] in their studies of the iron(III) and indium(III) halide complexes. Since these complexes are considerably stronger than the lanthanide complexes it would seem reasonable to assume that there should have been some evidence for the formation of higher order complexes.

Because of this discrepancy, it was at first suspected that the k_2 stability constant for the formation of MA_2^+ might be fictitious and the nonlinear behaviour caused by a change in the activity of water when changing the aqueous phase from 1 M $HClO_4$ to 1 M HCl. However, calculations indicate that the activity of H_2O is slightly greater in 1 M HCl than in 1 M $HClO_4$, which should cause the curve to deviate in a downward direction rather than upwards. Moreover, the change in the activity of water was so small (0.816 in 1 M HCl as compared to 0.810 in 1 M $HClO_4$), it seemed unlikely that it could account for the observed change in the distribution ratio.

To add further credulity to the formation of the complex MA_2^+ the extraction of ^{22}Na was studied using the same system as that employed with the lanthanide ions. If NaCl is assumed to be completely dissociated in aqueous solution any variation in the distribution ratio should be due to a change in the activity of hydrogen ion. As seen in Fig. 4, a plot of $1/K_d$ vs. [A] curves downwards, which is the trend predicted from the calculated change in the activity of water. From these arguments it is concluded that the complex MA_2^+ is formed in these systems and the actual value for k_2 is, perhaps, slightly larger than the calculated values due to the slight increase in the activity of water when changing the aqueous phase from 1 M $HClO_4$ to 1 M HCl.

The failure of WHITE et al. to obtain evidence for the higher order complexes is probably due to an insufficient number of points in the plot of $1/K_d$ vs. [A] and/or to the uncertainty in the values of their distribution rations. Their value for the precision in attaining the distribution ratio was ± 0.5 per cent. In comparing their alues for the k_1 stability constants of iron(III) and indium(III) chloride complexes ith those determined by other methods, it can be seen that their values are slightly rger. This is especially true in the experiments where the chloride ion concentration proaches 1 M. We, therefore, believe that their values for the k_1 stability constants

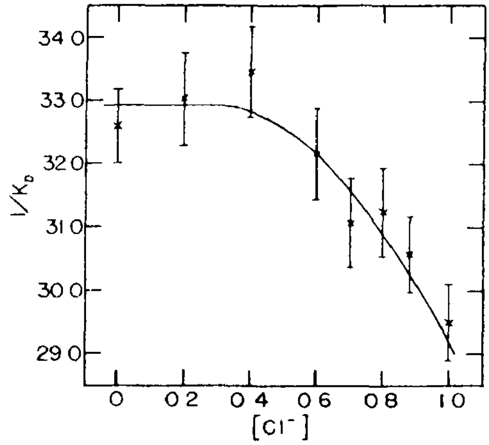


FIG. 5. Extraction of Na(I) at 25°C as a function of [Cl⁻] with 1.00 M ionic strength in the aqueous phase and 0.01 F HD in the organic phase.

determined in solutions of high ionic strengths (e.g., 1 M and 2 M) are too large due to the formation of the second complex MA_2. Indeed, in comparing the values of k_1 for the lanthanide halides in Tables 2 and 3, the difference in the values of k_1 as determined by the two methods is about 10 per cent, approximately the same difference between the values of k_1 determined by WHITE *et al.* and the values determined by other methods for $FeCl^{2+}$ and $InCl^{2+}$.

The thermodynamic functions for the formation of the complex $EuCl^{2+}$ were determined to investigate further the type of complex that is formed. The free energy change, ΔF, can be calculated directly from the stability constant. ΔH was determined by the temperature differential method by experimentally determining the stability constant at 0°, 25° and 48°C. The entropy change, ΔS, can be determined from the values of ΔF and ΔH at 25°C. These values of the thermodynamic functions were then converted to the unitary functions to correct for the numbers of interacting species in solution.⁽⁶⁾ The values of the unitary functions are listed in Table 4.

TABLE 4. UNITARY THERMODYNAMIC FUNCTIONS FOR THE COMPLEX $EuCl^{2+}$ AT 25°C

Complex	Ionic strength	Temperature	ΔF′ (kcal/mole)	ΔH′ (kcal/mole)	ΔS′ (e.u.)
$EuCl^{2+}$	1.0	25°C	2.29 ± 0.4	0.05 ± 0.03	3.0 ± 3.0

Since complex formation is favoured by positive entropy changes and negative heat changes,⁽⁷⁾ the formation of the complex $EuCl^{2+}$ is favoured by both heat and entropy changes, although both ΔH′ and ΔS′ are small, reflecting the weakness of the $EuCl^{2+}$ complex. For the formation of an inner sphere complex with the replacement of one mole of water the entropy change is usually about 16.7 e.u., while the heat change is between 0 and ±5 kcal/mole. Thus it is seen that both the entropy

---

⁽⁶⁾ R. GURNEY, *Ionic Processes in Solution*, McGraw-Hill, New York (1953).

⁽⁷⁾ F. J. C. ROSSOTTI, *Modern Coordination Chemistry* (Edited by J. LEWIS and R. G. WILKINS), Interscience, New York (1960).

and enthalpy changes are consistent with the view that $EuCl^{2}$ is weak ionic and an outer sphere complex However, the large error in $\Delta H'$ inherent in the temperature differential method and the consequent error in $\Delta S'$ do not allow an unambiguous assignment of the type of complex formed by the lanthanide halides

Acknowledgement –The financial assistance of the U S Atomic Energy Commission through Contract -AT(40-1)-1797 is gratefully acknowledged

J Inorg Nucl Chem, 1963 Vol 25 pp 395 to 405 Pergamon Press Ltd Printed in Northern Ireland

THE THERMAL DECOMPOSITION OF METAL COMPLEXES—II

SOME AMMINE AND ETHYLENEDIAMINE COMPLEXES OF NICKEL (II)*

T D GEORGI and W W WENDLANDT
Department of Chemistry, Texas Technological College
Lubbock, Texas

(*Received* 16 *August* 1962)

Abstract The thermal dissociation of some ammine and ethylenediamine complexes of nickel (II) were studied by the techniques of DTA, TGA, and GE The ammine complexes, $[Ni(NH_3)_6]X_2$ (where X Cl, Br, NO_3 and SO_4), dissociated in two steps, giving the intermediate complex, $[Ni(NH_3)_2]X_2$ (except NO_3) The *tris*(ethylenediamine)- complexes, $[Ni(en)_3]X_2$ (where X Cl, Br, I, NO_3 SO_4), lost the ethylenediamine step-wise, but not as distinctly as in the hexammine-complexes The order or increasing thermal stability for the $[Ni(NH_3)_6]X_2$ type complexes was NO_3 Cl SO_4 Br, for the $[Ni(en)_3]X_2$ type complexes, the order was Cl Br - NO_3 I SO_4 The thermal dissociation process for all of the complexes is discussed in detail

The hexamminenickel (II) complexes of the type, $[Ni(NH_3)_6]X_2$, have been extensively studied (1) However, since their first preparation by ROSE(2) and ERDMANN(3) in the 1834-1840 period, little is still known concerning their thermal properties Dissociation temperatures, in an atmosphere of ammonia, have been determined for several of the hexammine complexes (4,5) These temperatures, based on changes of pressure in the system, ranged from 176° to 235 5°C, for the chloride and iodide complexes, respectively The dissociation pressures of complexes containing oxyanions have also been determined (6) Even with the above studies, the thermal dissociation process is still not very well understood

Even less is known concerning the thermal dissociation of the *bis*-and *tris*(ethylenediamine) nickel (II) complexes These complexes, of the type $[Ni(en)_n]X_2$, were first prepared by WERNER(7) and have been rather extensively studied by other physicochemical methods (1) A preliminary study of the thermal dissociation of the ethylenediamine (en) and 1,2-propanediamine nickel (II) complexes, in an oxidizing atmosphere, has previously been described (8)

---

* Part I W W WENDLANDT, T D GEORGI and K V KRISHNAMURTY, *J Inorg Nucl Chem* **21**, 69 (1961)

(1) R DUVAL, *Nouveau Traite de Chimie Minerale* (Edited by P J PASCAL) Vol XVIII, pp 761-892 Masson et Cie, Paris (1959)

(2) H ROSE, *J Prakt Chem* **7**, 266 (1836)

(3) O L ERDMANN *J Prakt Chem* **1**, 266 (1834), **7**, 249 (1836) **19**, 445 (1840)

(4) W BILTZ and B FETKENHEUER *Z Anorg Chem* **83**, 163 (1913), **89**, 134 (1914)

(5) A B HART and J R PARTINGTON, *J Chem Soc* 104 (1943)

(6) F EPHRIAM and E MULLER, *Ber Dtsch Chem Ges* **54**, 973 (1921)

(7) A WERNER, *Z Anorg Chem* **21**, 199 (1899)

(8) T D GEORGI and W W WENDLANDT, *Tex J Sci* **14**, 47 (1962)

It is thus the object of this investigation to study the thermal dissociation of several hexammine- and *bis*- and *tris*(ethylenediamine)nickel (II) complexes by the techniques of thermogravimetric analysis (TGA), differential thermal analysis (DTA), and gas evolution analysis (GE), all in an inert atmosphere under carefully controlled conditions of pyrolysis.

EXPERIMENTAL

Apparatus

Thermobalance. An Ainsworth Type RV vacuum balance which could be operated under a dynamic nitrogen gas atmosphere was used for the TGA studies. Sample sizes ranged in weight from 10 to 15 mg. The furnace temperature controller has previously been described.[9] The temperature of the furnace chamber was monitored by a chromel-alumel thermocouple and recorded, along with the weight change, on a two-pen strip-chart recorder. A furnace heating rate of 7°C per min was employed.

DTA and GE apparatus. The DTA and GE apparatus used has previously been described.[10] Sample sizes ranged in weight from 50 to 75 mg and were pyrolysed under a dynamic helium gas atmosphere. The evolved gas concentration in the helium gas stream was detected by a thermistor thermal conductivity detector. Output signals from the DTA amplifier and GE detector were recorded as a function of temperature on two X-Y recorders. In all cases, a heating rate of 10 ± 1°C per min was employed. Previously ignited alumina was used as the reference material in the DTA sample block.

Gas samples from the GE detector were analyzed by mass spectrographic analysis using a Consolidated Engineering Corp. Model 21-602 mass spectrometer.

Chemicals

The nickel (II) compounds used were in the form of halides, nitrate, or sulphate and were obtained from the J. T. Baker Chemical Co., Phillipsburg, N.J. The ethylenediamine was obtained from the Eastman Organic Chemical Co., Rochester, N.Y. The other chemicals used were of C.p. quality.

Preparation of the complexes

The *tris*-(ethylenediamine)- and *bis*(ethylenediamine)nickel (II) complexes except for the *tris*-(ethylenediamine)nickel (II) sulphate, were prepared by the method given by STATE.[11] The sulphate was prepared by the method of WERNER, while the bromide was prepared as previously described.[8] The hexamminenickel(II) halide and nitrate complexes were prepared in a manner similar to that described by WYCOFF.[12] The sulphate was prepared by adding an excess of concentrated aqueous NH_3 to a saturated solution of $NiSO_4 \cdot XH_2O$ and precipitating out small violet-coloured crystals by the addition of 95 per cent ethanol. The hexammine-complexes were washed with ethanol and ether and then air dried.

The ethylenediamine-complexes were analysed by thermal decomposition to the metal oxide in an air atmosphere on a thermobalance. The hexammine-complexes were analysed in a similar manner by thermal decomposition to the respective parent salts, with the exception of the nitrate, in an atmosphere of nitrogen.

DISCUSSION

A. *Weight-loss studies*

The weight-loss curves, in nitrogen, for the hexammine-complexes are given in Fig. 1 while the weight-loss data are given in Table 1.

The hexamminenickel (II) chloride and bromide compounds appear to decompose in two rather distinct steps. The first step, which corresponded to the loss of four moles

---

[9] W. W. WENDLANDT, *J. Chem. Educ.* **38**, 571 (1961).

[10] W. W. WENDLANDT, *Anal. Chim. Acta* **27**, 309 (1962).

[11] H. M. STATE, *Inorganic Syntheses*, (Edited by L. G. ROCHOW) Vol. 6, p. 200. McGraw-Hill, New York (1960).

[12] R. W. G. WYCOFF, *J. Amer. Chem. Soc.* **44**, 1239 (1922).

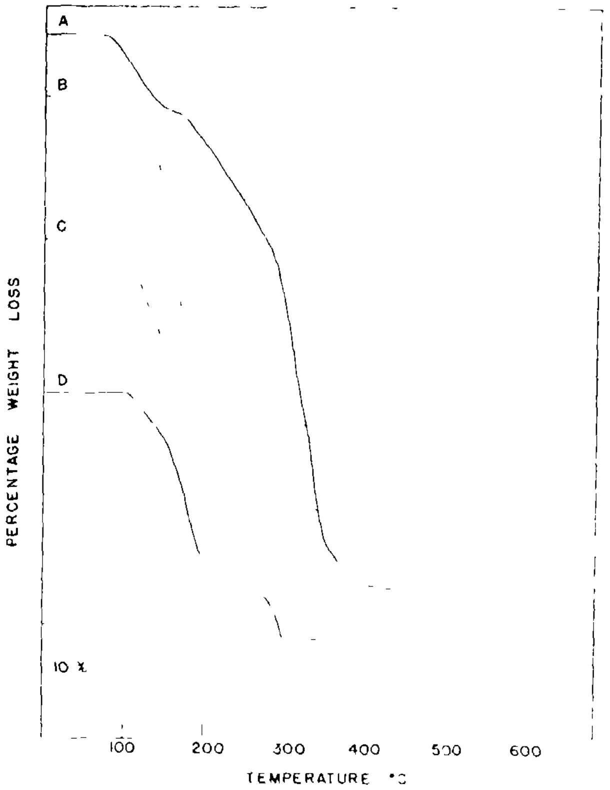


FIG. 1 Weight-loss curves of hexamminenickel complexes (under nitrogen) A $[Ni(NH_3)_6](NO_3)_2$, B $[Ni(NH_3)_6]Cl_2$, C $[Ni(NH_3)_6]SO_4$, D $[Ni(NH_3)_6]Br_2$

TABLE I COMPOSITION DATA FOR NICKEL (II) COMPLEXES

Compound	NiO (%) Calc	NiO (%) Found	H_2O (%) Calc	H_2O (%) Found	NH_3 (%) Calc	NH_3 (%) Found
$[Ni(en)_3]Cl_2 \cdot 2H_2O$	21.59	22.1	10.45	11.0		
$[Ni(en)_3]Br_2 \cdot 2H_2O$	17.17	17.6	8.47	8.5		
$[Ni(en)_3]I_2$	15.17	15.7				
$[Ni(en)_3](NO_3)_2$	20.60	21.2				
$[Ni(en)_3]SO_4$	22.25	22.6				
$[Ni(en)_2]Cl_2$	29.95	30.4				
$[Ni(en)_2]Br_2$	22.10	22.2				
$[Ni(NH_3)_6]Cl_2$					44.08	44.1
$[Ni(NH_3)_6]Br_2$					31.86	31.8
$[Ni(NH_3)_6]SO_4$					39.77	39.7
$[Ni(NH_3)_6](NO_3)_2$	26.22	26.7				

$[Ni(NH_3)_6]X_2$,		Loss of $4NH_3$ (%) Calc	Found
X	Cl	29.39	28.8
	Br	21.24	21.5
	SO_4	26.51	26.6

of ammonia per mole of compound, began at about 85 and 105°C, for the chloride and bromide complexes respectively. The second step, the loss of the two remaining moles of ammonia, began immediately after the first step at temperatures of 175 and 195°C respectively. Thus, for these two compounds, the thermal dissociation follows the equations

$$[Ni(NH_3)_6]X_2(s) \rightarrow [Ni(NH_3)_2]X_2(s) + 4NH_3(g)$$

$$[Ni(NH_3)_2]X_2(s) \rightarrow NiX_2(s) + 2NH_3(g)$$

This is confirmed quantitatively by the weight-loss data in Table I and qualitatively for ammonia by mass spectrographic analysis. No other gaseous decomposition products were detected.

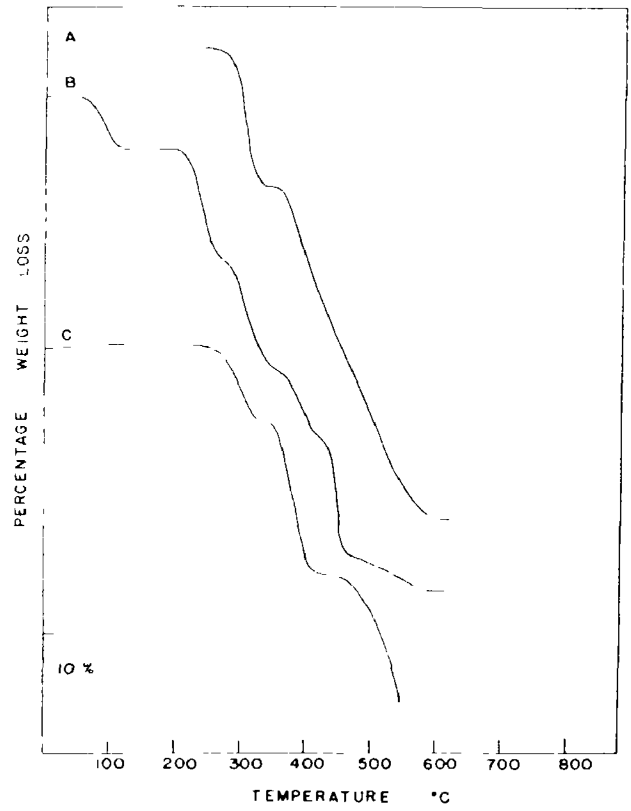


FIG. 2 Weight-loss curves of *bis*- and *tris*(ethylenediamine)nickel complexes (under nitrogen) A $[Ni(en)_2]Cl_2$, B $[Ni(en)_3]Cl_2 \cdot 2H_2O$, C $[Ni(en)_3]I_2$

The complex, $[Ni(NH_3)_6]SO_4$, also decomposed by a two-step process, but the second step was not as distinct as in the case of the chloride and bromide. This compound began to decompose at about 90°C and showed a definite break in the curve at about 180°C. The weight loss up to this point corresponded to the loss of four moles of ammonia per mole of compound. The second step of the decomposition resulted in the gradual loss of the remaining two moles of ammonia and the formation of $NiSO_4$ at about 530°C.

The complex, $[Ni(NH_3)_6](NO_3)_2$, began to decompose at about 80°C and gave the oxide level about 420°C inflexion in the weight-loss curve occurred at about 150 C and approximated the loss of two moles of ammonia per mole of complex In view of the fact that the complex contains oxidizing (nitrate) as well as reducing groups (ammonia), this behaviour was not unexpected The decomposition reaction is definitely different from the other hexammine complexes

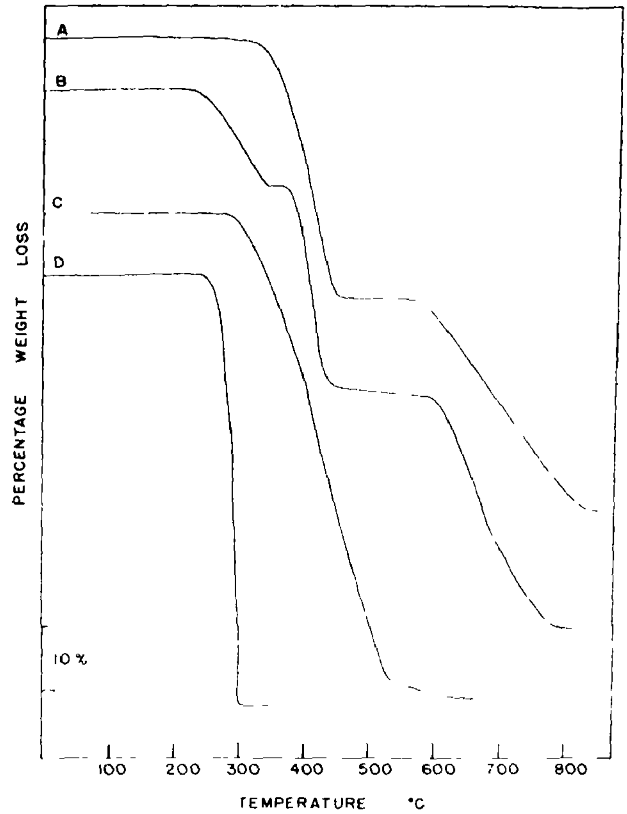


FIG. 3 Weight-loss curves of *bis*- and *tris*(ethylenediamine)nickel complexes (under nitrogen) A $[Ni(en)_2]Br_2$, B $[Ni(en)_3]Br_2$, C $[Ni(en)_3]SO_4$, D $[Ni(en)_3](NO_3)_2$

The thermograms for the decomposition of *tris*(ethylenediamine)- and *bis*(ethylenediamine)-nickel(II) compounds, in nitrogen, are given in Fig 2 and 3 while the weight-loss data are given in Table I

There was no general dissociation pattern which could be applied to all of the *tris* (ethylenediamine)nickel(II) complexes The one generalization which can be made, however, is that all of the complexes showed an inflection in the weight-loss curve which corresponded closely to the loss of one mole of ethylenediamine per mole of compound Other inflexions found on the weight-loss curves were, however rather indefinite and in many cases, corresponded to no known stoicheiometric compounds

In the process of evacuating the thermobalance system before flooding with nitrogen gas the $[Ni(en)_3]Br_2\,2H_2O$ lost all of its water of hydration and formed the anhydrous compound The hydrated chloride, $[Ni(en)_3]Cl_2\,2H_2O$, appeared to be more stable in that it retained its water of hydration during the balance evacuation period This latter compound began to evolve water at about 55 C, and gave the anhydrous weight level at about 115 C All of the anhydrous *tris*(ethylenediamine) complexes began to evolve ethylenediamine in the temperature range of 200 to 300 C

The anhydrous [Ni(en)$_3$]Cl$_2$ gave an inflexion point at about 250 C which corresponded to the approximate loss of one mole of ethylenediamine per mole of complex and the formation of [Ni(en)$_2$]Cl$_2$ This is roughly confirmed by the TGA curve for [Ni(en)$_2$]Cl$_2$ This latter complex began to decompose at about same temperature as the inflection point in the former complex Other inflexion point were found in the [Ni(en)$_3$]Cl$_2$ curve at 350 and 420 C The former approximated the loss of two moles and the latter of three moles of ethylenediamine Beyond 420 C the weight-loss was due to the sublimation of nickel(II) chloride It is of interest to note that the *bis*(ethylenediamine) complex lost weight continuously beyond the 400 C inflexion point

The anhydrous bromide complex, [Ni(en)$_3$]Br$_2$, began to decompose at about 250 °C A horizontal weight level was observed between 380 and 400 C which corresponded to the composition, [Ni(en)$_2$]Br$_2$ This intermediate complex appeared to be more stable than the corresponding [Ni(en)$_2$]Cl$_2$ complex There was no inflexion observed in the curve which indicated the loss of a second mole of ethylenediamine The next horizontal weight level occurred at about 450 C and corresponded to the loss of the remaining two moles of ethylenediamine and the formation of NiBr$_2$ Here as in the case of [Ni(en)$_3$]Cl$_2$ 2H$_2$O further weight-loss was observed and was attributed to the sublimation of NiBr$_2$

The compound, [Ni(en)$_3$]I$_2$ began to decompose at about 260 C and gave an inflexion in the curve at 340 C which approximated the composition, [Ni(en)$_2$]I$_2$ The next curve inflexion at 430 C corresponded to the loss of all three moles of ethylenediamine and the formation of NiI$_2$ Again, sublimation of the nickel salt was observed

The weight-loss curves for [Ni(en)$_3$]SO$_4$ and [Ni(en)$_3$](NO$_3$)$_2$ both showed a one step decomposition reaction The sulfate began to decompose at about 310 C and gave a horizontal weight level beginning at about 640 C Calculations from the weight-loss at this point indicated the stoicheiometry for NiO The complex, [Ni(en)$_3$](NO$_3$)$_2$, began to decompose at about 250 C and resulted in the formation of NiO at about 300 C

The *bis*(ethylenediamine)nickel (II) chloride and bromide complexes gave weight-loss curves which approximated those of the corresponding *tris*(ethylenediamine) complexes, after the loss of one mole of ethylenediamine

B DTA *and* GE *studies*

The DTA and GE curves for the hexamminenickel (II) complexes are given in Fig 4 and 5

The interpretation of the DTA curves for the above complexes presents a number of problems These problems are similar to those found for the metal salt hydrate systems(13, 14) in which endothermic peaks were found which were caused by reactions of the type $MX_2\,nH_2O \rightarrow MX_2(n-m)H_2O + mH_2O(l)$ followed by $mH_2O(l) \rightarrow mH_2O(v)$ The reactions above can be completely misinterpreted on the basis of DTA

---

(13) H J Borchardt and F Daniels, *J Phys Chem* **61**, 917 (1957)

(14) A Reisman and J Karlak, *J Amer Chem Soc* **80**, 6500 (1958)

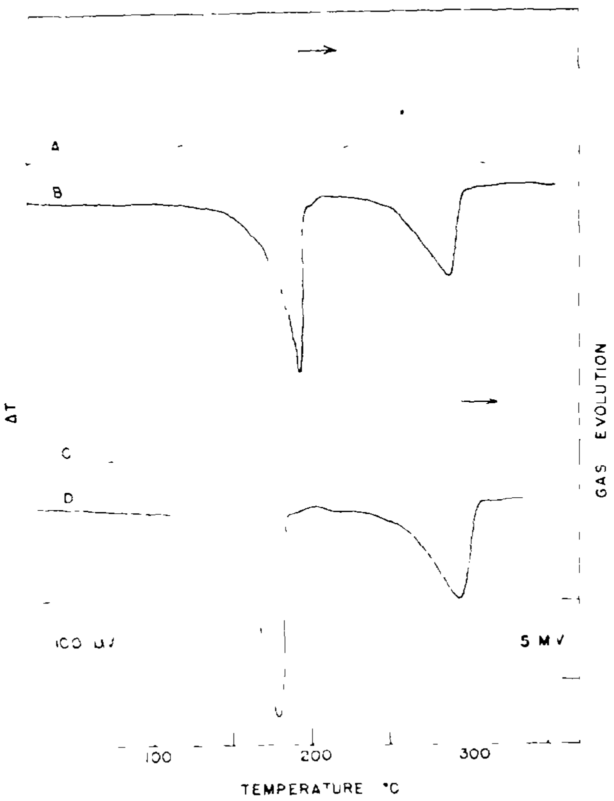


FIG. 4. DTA and GE curves of hexamminenickel complexes (under helium)
A and B $[Ni(NH_3)_6]Br_2$. C and D $[Ni(NH_3)_6]Cl_2$.

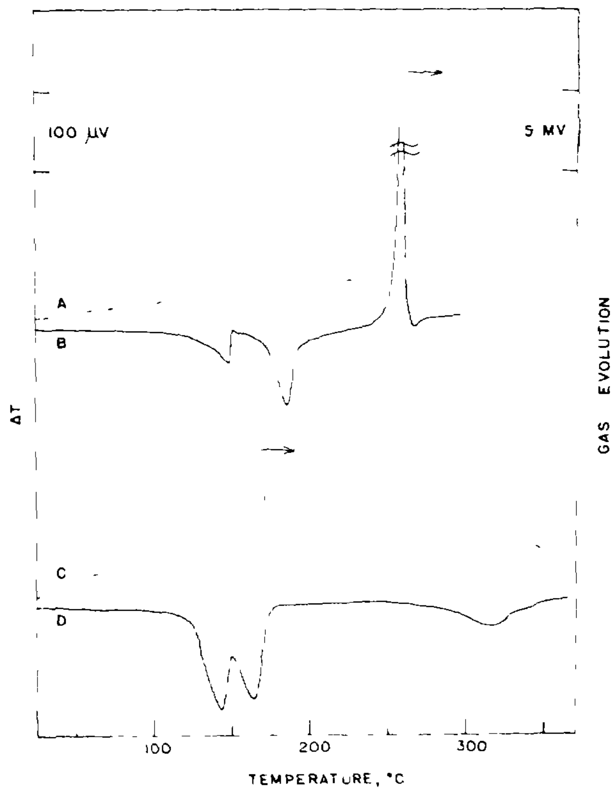


FIG. 5. DTA and GE curves of hexamminenickel complexes (under helium)
A and B $[Ni(NH_3)_6](NO_3)_2$. C and D $[Ni(NH_3)_6]SO_4$.

alone This misinterpretation is much less probable, however, if the DTA data is supplemented by other information such as TGA, X-ray diffraction, GE, analysis of decomposition gases and so on In this investigation, the interpretation of the DTA data is based not only on the curve itself but on the supplementary data as well

The hexamminenickel (II) chloride and bromide gave similar DTA and GE curves

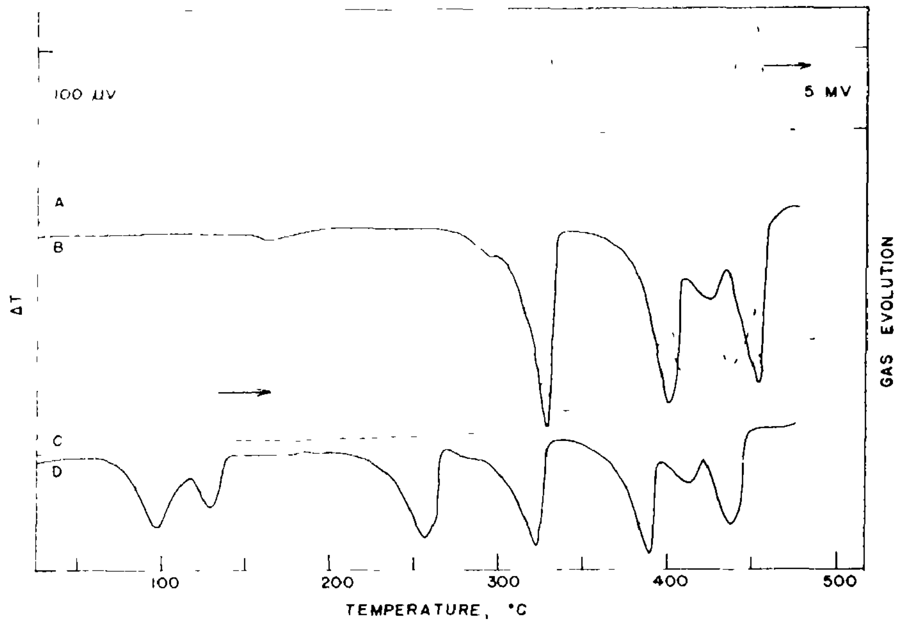


FIG. 6 DTA and GE curves of *bis*- and *tris*(ethylenediammine)nickel complexes (under nitrogen) A and B $[Ni(en)_2]Cl_2$ C and D $[Ni(en)_3]Cl_2 \, 2H_2O$

The first peak corresponded to the loss of four moles of ammonia per mole of complex, while the second peak corresponded to the loss of the other two moles of ammonia The evolution of ammonia was confirmed by mass spectrographic analysis of the furnace gas stream This decomposition reaction corresponds to that found by the TGA studies

The complex, $[Ni(NH_3)_6]SO_4$, gave three endothermic peaks, at 145, 165 and 315°C, respectively The first two peaks were caused by the evolution of four moles of ammonia per mole of compound while the last peak was due to the evolution of the remaining two moles of ammonia The broad peak of the latter revealed the rather slow decomposition reaction as shown in the TGA curve Mass spectrographic analysis of the evolved gases indicated that only ammonia was evolved

A rather interesting DTA curve resulted from the thermal decomposition of $[Ni(NH_3)_6](NO_3)_2$ The compound gave two endothermic peaks, at 150° and 185°C, respectively, which were caused by the evolution of between two and three moles of ammonia per mole of complex This amount of ammonia was determined by collection of the evolved gas in a standard hydrochloric acid solution The ammonia to nickel ratio found as 2 76 1 On continued heating, the compound decomposed violently, as evidenced by the exothermic peak at 260°C Mass spectrographic analysis showed only nitrogen, water and oxygen in the decomposition gases Not enough information was available, however, to give the complete stoichiometry for the reaction

The DTA and GE curves for the *bis*- and *tris*(ethylenediamine)nickel(II) complexes are given in Figs 6–8

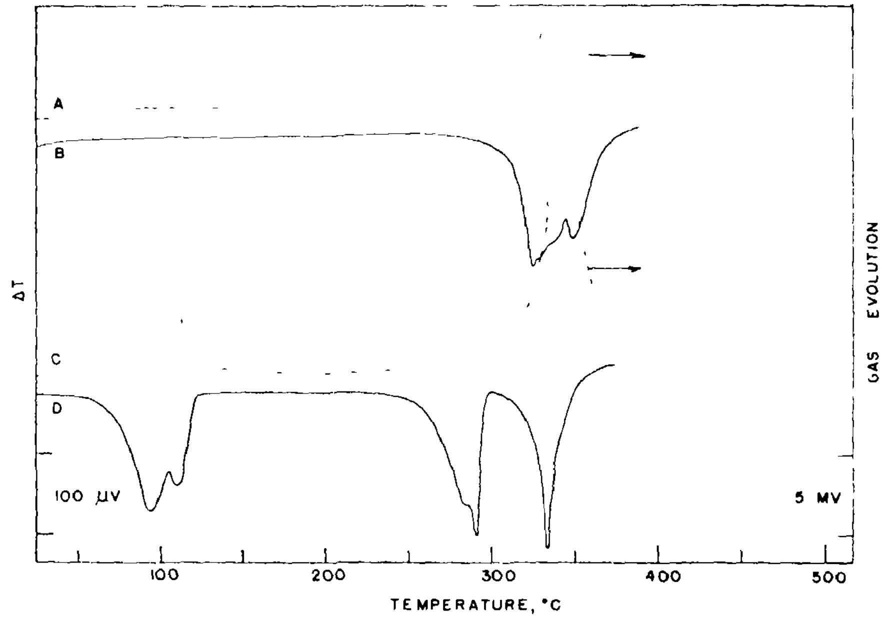


FIG 7 —DTA and GE curves of *bis*- and *tris*(ethylenediamine)nickel complexes (under helium) A and B $[Ni(en)_2]Br_2$, C and D $[Ni(en)_3]Br_2 \cdot 2H_2O$

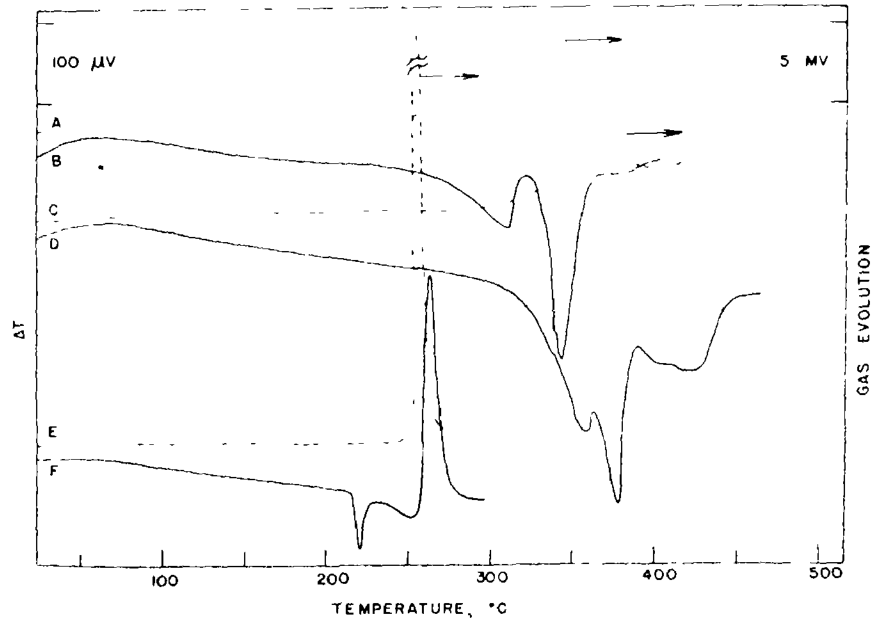


FIG. 8 DTA and GE curves of *tris*(ethylenediamine)nickel complexes (under helium) A and B $[Ni(en)_3]I_2$ C and D $[Ni(en)_3]SO_4$, E and F $[Ni(en)_3](NO_3)_2$

The complex $[Ni(en)_3]Cl_2 \cdot 2H_2O$ gave only endothermic peaks. The first two peaks at 95 and 130°C respectively corresponded to the loss of the two moles of hydrate water per mole of complex. The DTA results indicated that the dehydration was a two-step rather than a one-step process as indicated by the weight-loss curve. The anhydrous compound was stable up to about 225°C where a third endothermic peak began having a peak maxima temperature of about 255°C. However, a gas evolution peak was not detected in this temperature range although from TGA data there was a definite weight-loss. The only conclusion which can be drawn from this behaviour is that: (a) a crystalline phase transition or thermal rearrangement has occurred; or (b) the loss of ethylenediamine (liquid), according to the reaction

$$[Ni(en)_3]Cl_2(s) \rightarrow [Ni(en)_2Cl_2(s) + en(l)$$

has taken place. This latter behaviour would be similar to that found in several metal salt hydrate systems.[13] Such a reaction is possible if the system has a quadruple point where the amine, next lower amine, saturated solution and ethylenediamine vapour are in equilibrium and if this point occurs at an ethylenediamine vapour pressure which is less than atmosphere (in this case ~680 mm).

The next endothermic peak at 320°C, if the latter assumption is correct, would correspond to the thermal effect due to the reaction

$$en(l) \rightarrow en(v)$$

plus the deamination of $[Ni(en)_2]Cl_2$. The curve for the *bis*-(ethylenediamine) compound gave a similar endothermic peak at 330°C which was due to deamination reaction. A GI peak was also observed for the latter compound at this temperature. The last series of endothermic peaks at 390, 415 and 440°C, respectively, were attributed to the loss of the last mole of ethylenediamine and the formation of $NiCl_2$. The endothermic peak at 440°C corresponded to the region on the weight-loss curve which showed that three moles of ethylenediamine had been evolved. It is apparent that the loss of the third mole of ethylenediamine is not a one-step process. Gas samples were collected for each of the peaks and analyzed on the mass spectrograph. The endothermic peaks at 95 and 130°C indicated the loss of water, while the remainder of the peaks showed only the evolution of ethylenediamine.

The complex, $[Ni(en)_3]Br_2 \cdot 2H_2O$, gave endothermic peaks at 95, 110, 290 and 335°C. The first two peaks were caused by the loss of the two moles of hydrate water. Comparison with the weight-loss curves indicated that the endothermic peak at 290°C resulted from the loss of one mole of ethylenediamine per mole of complex, while the second endothermic peak at 335°C resulted from the loss of two additional moles of ethylenediamine and the formation of $NiBr_2$. Analysis on the mass spectrometer of gas samples collected for each of these peaks confirmed these results.

The complex, $[Ni(en)_3]I_2$, gave only two endothermic peaks, as was expected from the weight loss studies. The first endothermic peak at 325°C was attributed to the loss of one mole of ethylenediamine, while the second peak at 345°C resulted from the loss of the other two moles of ethylenediamine.

The complex, $[Ni(en)_3]SO_4$, gave three endothermic peaks, at 360, 380 and 425°C, respectively. In each case there was evidence of the evolution of gas. The origin of each of the peaks is not known specifically as the weight-loss curve indicates a continuous loss of weight to the oxide level at about 650°C. Temperature limitations of the DTA apparatus prevented study above about 450°C.

The complex, $[Ni(en)_3](NO_3)_2$, gave an endothermic peak at 220 C and an exothermic peak at 265 C The endothermic peak gave no evidence of gas evolution and possibly resulted from a crystalline phase transition of some type The exothermic peak resulted from the violent decomposition of the complex with resultant formation of NiO

The two *bis*(ethylenediamine) complexes decomposed in a manner similar to the *tris*(ethylenediamine complexes, after the loss of the first mole of ethylenediamine In the case of the chloride, the same peaks were present in the curve but were shifted to slightly higher temperatures The bromide complex decomposed giving a rather broad peak while the *tris*(ethylenediamine) complex exhibited a sharper peak for the same decomposition reaction The reason for this behavior is not known

C *General*

If the minimum TGA decomposition temperatures are taken as a rough criteria for the thermal stability of these complexes, the order of increasing stability for the hexammine-complexes was NO_3 Cl SO_4 Br For the loss of the remaining two moles of ammonia, the order of increasing stability was Cl SO_4 Br For the *tris*(ethylenediamine) complexes, the order of increasing stability was Cl Br $NO_3 <$ I SO_4 The order of increasing thermal stability in an oxidizing atmosphere[(8)] was only slightly different or Cl I Br NO_3 SO_4 indicating that the iodide was much less stable Thus, it appears that the initial decomposition reaction is not one of oxidation but of thermal dissociation only The iodide complex is an exception due to the ease of formation of free iodine From previous studies on the *tris*(ethylenediamine)copper(II) sulphate,[(10)] it is seen that the corresponding nickel complex is more stable, 310 vs 200 C for the copper complex

The ethylenediamine metal chelates, as was expected, were more stable than the hexammine complexes In almost every case the latter complexes decomposed at a temperature one-half to one-third that found for the former This increased stability of ethylenediamine nickel chelates over the ammine complexes is also shown by calorimetric heat-of-reaction data[(15,16)]

Acknowledgement This work was supported by a grant from the Organized Research Fund of Texas Technological College

---

(9) I Poulsen and J Bjerrum *Acta Chem Scand* **9**, 1407 (1955)

(10) K B Yatsimirskii and P M Nilyukov *Zh fiz Khim* **31**, 842 (1947)

J. Inorg. Nucl. Chem. 1963. Vol. 25, pp. 407 to 414. Pergamon Press Ltd. Printed in Northern Ireland

A BASIS FOR THE PREDICTION OF THE THERMAL DECOMPOSITION PRODUCTS OF METAL PERCHLORATES

M. M. MARKOWITZ
Foote Mineral Company, Research and Engineering Centre, Chemicals Division
Route 100, Exton, Penna

(*Received* 4 *June* 1962, *in revised form* 6 *August* 1962)

Abstract—Depending on the cation, a metal perchlorate may decompose to yield the corresponding oxide or chloride. Accordingly, a systematic basis for predicting and rationalizing the reaction products of decomposing hydrated and anhydrous perchlorates is evolved by consideration of the relative values of the equivalent free energies of formation of the possible reaction products (oxides or chlorides). A review of those metal perchlorates already studied demonstrates the validity of this approach. Magnesium perchlorate represents an intermediate case in the treatment because of the comparable free energies of formation of the oxide and chloride. As a result, it is experimentally confirmed that a mixture of the two materials is obtained on pyrolyzing magnesium perchlorate. Below 427°, the formation of magnesium oxide appears to be due to an internal oxygenation reaction $MgCl_2$ (solid) + $\frac{1}{2}O_2$ (gas) → MgO (solid) + Cl_2 (gas). If the free energy data are not available, the equivalent enthalpies of formation of the possible reaction products may be used as guides to formulating the expected preponderant reaction residues.

DESPITE wide variations in the sizes, electronegativities, and polarizing powers of the cations, and crystal structures and phase changes of metal perchlorate salts, these compounds generally achieve significant rates of decomposition below 600°. However, depending on the cation (M^{n+}), the residual product of pyrolysis of a hydrated or anhydrous metal perchlorate may be preponderantly a chloride as formed by the overall reaction

$$M^{n+}(ClO_4)_n \cdot xH_2O \rightarrow M^{n+}Cl_n + 2nO_2 + xH_2O, \quad x = 0, 1 \tag{1}$$

or the residue may be substantially an oxide as generated through the summary equation

$$M^{n+}(ClO_4^-)_n \cdot xH_2O \rightarrow \tfrac{1}{2}M_2^{n+}O_n + \frac{n}{2}Cl_2 + 1.75nO_2 + xH_2O, \quad x = 0, 1 \tag{2}$$

The pyrolytic behaviour of metal perchlorates is unique when compared to the decompositions of other metal compounds containing decomposable polyatomic anions, e.g., the metal nitrates,(1,2) carbonates,(3) sulphates(4,5) and hydroxides,(5,6) which all ultimately decompose unambiguously to the corresponding oxide or free metal (if for example, as in the case of silver oxide,(7,8) the oxide is unstable at elevated temperatures). Thus, the present study is an attempt to explore the duality of possible

---

(1) M. Centnerszwer, *Rocz. Chem.* **19**, 419 (1938).
(2) N. V. Sidgwick, *The Chemical Elements and Their Compounds*, Vol. I, pp. 700–701. Oxford (1950).
(3) A. E. van Arkel, *Molecules and Crystals in Inorganic Chemistry*, pp. 118–119. Butterworths, London (1949).
(4) A. G. Ostroff and R. T. Sanderson, *J. Inorg. Nucl. Chem.* **9**, 45 (1959).
(5) R. T. Sanderson, *Chemical Periodicity*, pp. 162–165. Reinhold, New York (1960).
(6) H. L. Johnston and T. W. Bauer, *J. Amer. Chem. Soc.* **73**, 1119 (1951).
(7) G. N. Lewis, *Z. Phys. Chem.* **52**, 310 (1905).
(8) P. J. Herley and E. G. Prout, *J. Amer. Chem. Soc.* **82**, 1540 (1960).

thermal decomposition products of perchlorates and to devise a basis on which the nature of the final pyrolysis products of metal perchlorates can be anticipated as a function of temperature.

The hydrated ($LiClO_4 \cdot xH_2O$, x = 1, 3; $NaClO_4 \cdot H_2O$) and anhydrous alkali metal perchlorates all decompose predominantly following Equation (1),(9, 10, 11) as do both calcium (x = 0, 4),(12) barium (x = 0, 3)(12) and silver perchlorates (x = 0).(13, 14) Hydrated aluminum (x = 6)(12, 15) and ferric (x = 6)(15) perchlorates, on the other hand, follow Equation (2). Magnesium perchlorate (x = 0, 6)(12, 15) appears to represent a transitionary case because a mixture of both magnesium oxide and chloride is found to occur as the final reaction product. Disruption of the perchlorate group can be concomitant with dehydration and hydrolysis reactions as probably take place with the hydrated perchlorates of the weaker bases,(12, 15) e.g., Fe^{3+} and Al^{3+}.

Thermodynamics of metal perchlorate decompositions

There is a paucity of free energy data pertaining to the metal perchlorates. However, numerical data are available(16) for the standard free energies of formation at 25° of potassium (72.7 kcal/mole), rubidium (73.2 kcal/mole) and cesium (73.3 kcal/mole) perchlorates. It is instructive to compute the changes in enthalpy (ΔH°), entropy (ΔS°) and free energy (ΔF°) corresponding to the following reactions at 25°:

$$MClO_4\,(\text{solid}) \rightarrow MCl\,(\text{solid}) + 2O_2\,(\text{gas}) \quad \text{and} \tag{3}$$

$$MClO_4\,(\text{solid}) \rightarrow \tfrac{1}{2}M_2O\,(\text{solid}) + \tfrac{1}{2}Cl_2\,(\text{gas}) + \tfrac{7}{4}O_2(\text{gas}) \tag{4}$$

where M = K, Rb, Cs.

TABLE 1. THERMODYNAMIC CHANGES INVOLVED IN THE DECOMPOSITIONS OF THE ALKALI METAL PERCHLORATES AT 25°

Reaction	ΔF°_{298} (kcal/mole)		ΔH°_{298} (kcal/mole)		ΔS°_{298} (cal/mole °)	
K (3, 4)	25.0	34.2	0.7	61.1	86.2	90.2
Rb (3, 4)	25.3	38.4	1.0	64.1	88.2	87.2
Cs (3, 4)	26.2	41.3	0.4	65.9	89.2,	82.5
Li (3, 4)			6.0,	20.5		
Na (3, 4)			6.0	42.5		

For the first three materials of Table 1, reaction (3) is clearly favoured thermodynamically and is known to be predominant kinetically. Though the free energy changes for the alternate states of decomposition of lithium and sodium perchlorates are not known, differential thermal analysis (DTA) studies(9, 17) have shown their pyrolysis reactions to be exothermic. This behaviour is then thermodynamically consistent with reaction (3) as being favoured.

---

(9) M. M. MARKOWITZ, D. A. BORYTA and R. F. HARRIS, *J. Phys. Chem.* **65**, 261 (1961).

(10) M. M. MARKOWITZ and D. A. BORYTA, *Analyt. Chem.* **32**, 1588 (1960).

(11) M. M. MARKOWITZ and D. A. BORYTA, Unpublished results.

(12) A. A. ZINOV'EV and L. I. CHUDINOVA, *Zh. Neorg. Khim.* **1**, 1722 (1956).

(13) S. GORDON and C. CAMPBELL, *Analyt. Chem.* **27**, 1102 (1955).

(14) M. M. MARKOWITZ, *J. Phys. Chem.* **61**, 505 (1957).

(15) G. G. MARVIN and L. B. WOOLAVER, *Analyt. Chem.* **17**, 474 (1945).

(16) F. D. ROSSINI, D. D. WAGMAN, W. H. EVANS, S. LEVINE and I. JAFFE, *Selected Values of Chemical Thermodynamics Properties*, National Bureau of Standards Circular 500, U.S. Government Printing Office, Washington, D.C. (1952).

(17) M. M. MARKOWITZ and D. A. BORYTA, *J. Phys. Chem.* **64**, 1711 (1960).

Only a single compound is among each set of reaction products of Equations (3) and (4), the remaining products being elemental gaseous substances. The alternate formulation of reactions (1) and (4) as $2M^{n+}(ClO_4)_n \rightarrow M_2^{n}O_n + nCl_2O_7$ does not appear justified because of the established instability of dichlorine heptoxide even at room temperature.[18] It is clear that $\Delta F^\circ_{\text{reac }3} = \Delta F^\circ_{MCl} - \Delta F^\circ_{MClO_4}$, and $\Delta F^\circ_{\text{reac }4} = \frac{1}{2}\Delta F^\circ_{M_2O} - \Delta F^\circ_{MClO_4}$. Now, $\Delta F^\circ_{\text{reac }3} < \Delta F_{\text{reac }4}$, which is true by virtue of the inequality $\Delta F_{MCl} < \frac{1}{2}\Delta F_{M_2O}$. Thus, the decomposition reaction actually observed tends to proceed in the direction yielding the product of lower equivalent free energy of formation (i.e., $\Delta F^\circ_{\text{equiv}} = \Delta F^\circ_{\text{formation}}/n\nu$, n = valence of cation, and $\nu = 1$ for chloride and $\nu = 2$ for oxide).

Inspection of Table 2 (appropriate data collected from References (16), (19) and (20)) confirms that the relative values of the equivalent free energies of formation of the chloride and oxide determine the ultimate reaction products. In each instance, except for magnesium perchlorate, the differences in $\Delta F^\circ_{\text{equiv}}$ are consistently large and negative in the direction of the realized decomposition products over the temperature range from 25–627°. Indeed, for each perchlorate in Table 2 but magnesium perchlorate, the reaction residue could be predicted from the difference in $\Delta F^\circ_{\text{equiv}}$ of the chloride and oxide at 25°.

TABLE 2.—DIFFERENCES IN THE EQUIVALENT FREE ENERGIES AND ENTHALPIES OF FORMATION OF VARIOUS OXIDES AND CHLORIDES

Perchlorate salt	Known decomp product	$(\Delta F^\circ_{Cl} - \Delta F^\circ_{O})_{\text{equiv}}$ 25	427	627	$(\Delta H^\circ_{Cl} - \Delta H^\circ_{O})_{\text{equiv}}$ 25
$LiClO_4 \cdot xH_2O$ $x = 0, 1, 3$	LiCl	25.0	23.1	22.9	26.5
$NaClO_4 \cdot xH_2O$ $x = 0, 1$	NaCl	46.8	44.7	43.3	48.5
$KClO_4$	KCl	−59.4	57.4	−56.4	−60.8
$RbClO_4$	RbCl	63.7	61.8	−60.2	−63.4
$CsClO_4$	CsCl	67.0	66.0	65.0	65.6
$AgClO_4$	AgCl	24.9	22.6	23.0	26.8
$Al(ClO_4)_3 \cdot 6H_2O$	Al_2O_3	12.2	14.6	11.3	11.2
$Fe(ClO_4)_3 \cdot 6H_2O$	Fe_2O_3	+5.5	5.1	4.9	0.7
$Mg(ClO_4)_2 \cdot xH_2O$ $x = 0, 6$	MgO and $MgCl_2$ mixture	2.8	0.0	1.4	−4.8
$Ca(ClO_4)_2 \cdot xH_2O$ $x = 0, 4$	$CaCl_2$	18.0	16.2	15.6	−19.7
$Ba(ClO_4)_2 \cdot xH_2O$ $x = 0, 3$	$BaCl_2$	38.7	31.8	30.5	36.1

As a general rule it would appear that the nature of the major pyrolysis product of a metal perchlorate depends on the relative ionic characteristics of the chloride and oxide. Consequently, most polyvalent metal perchlorates, except those alkaline earths following magnesium, would be expected to yield the corresponding oxides on decomposing rather than the chlorides which tend to display marked covalent properties (e.g., $AlCl_3$ and $FeCl_3$). This trend in observed reaction product distribution is also consistent with the generally lower base strengths of many polyvalent metals On the basis of the free energy criteria proposed here, the perchlorates of beryllium(II), zinc(II) lanthanum(III), and thorium(IV) would be expected to yield the oxides on pyrolysis while the perchlorates of mercury(II), cobalt(II), and cadmium(II) would yield the corresponding chlorides on thermal decomposition Cupric perchlorate, like magnesium perchlorate, appears to be an intermediate case in which a mixture of oxide and chloride is to be expected as a result of decomposition

---

[18] C. C. ADDISON in Mellor's *Comprehensive Treatise on Inorganic and Theoretical Chemistry* Supplement II, Part I, p. 542. Longmans, Green, New York (1956).

[19] C. J. SMITHELLS, *Metals Reference Book*, Vol. 2, pp. 590–591, 596–598. Interscience, New York (1955).

[20] J. P. COUGHLIN, *Contributions to the Data on Theoretical Metallurgy XII. Heats and Free Energies of Formation of Inorganic Oxides*, Bureau of Mines Bulletin 542, U.S. Government Printing Office, Washington, D.C. (1954).

The thermal decomposition of magnesium perchlorate

Because of the comparable free energies of formation of magnesium chloride and oxide (Table 2) at decomposition temperatures, the product distribution cannot be unambiguously determined through application of the foregoing treatment An early thermogravimetric analysis (TGA) study(15) of magnesium perchlorate hexahydrate had led to the interpretation that magnesium oxide was formed due to sequential hydrolysis and dehydroxylation reactions

$$Mg(ClO_4)_2{\cdot}6H_2O \rightarrow Mg(OH)_2 + 2HClO_4 + 4H_2O \qquad (5)$$

$$Mg(OH)_2 \rightarrow MgO + H_2O \qquad (6)$$

However this reaction course does not appear likely in view of the facts that pure anhydrous magnesium perchlorate is actually prepared by dehydration of the hydrate at elevated temperatures (150–300°)(21) that from more recent DTA and gas evolution studies(12) it has been determined that a long temperature interval exists between dehydration (141–185°) and the onset of rapid perchlorate decomposition (410°), that the same product distribution is obtained from hydrated or anhydrous magnesium perchlorate(12) and finally, that magnesium hydroxide would not be expected to decompose completely in ambient air at moderate temperatures because of the low dissociation pressure of water shown by magnesium hydroxide (10 mm at 300°)(22) Two possible decomposition reactions may be formulated following Equations (1) and (2) These reactions are

$$Mg(ClO_4)_2\,(\text{solid}) \rightarrow MgCl_2\,(\text{solid}) + 4O_2\,(\text{gas}) \qquad (7)$$
$$\Delta F^\circ_{\text{reac }7} = \Delta F^\circ_{MgCl_2} - \Delta F^\circ_{Mg(ClO_4)_2}$$

and

$$Mg(ClO_4)_2\,(\text{solid}) \rightarrow MgO\,(\text{solid}) + Cl_2\,(\text{gas}) + \tfrac{7}{2}O_2\,(\text{gas}) \qquad (8)$$
$$\Delta F^\circ_{\text{reac }8} = \Delta F^\circ_{MgO} - \Delta F^\circ_{Mg(ClO_4)_2}$$

Because the free energies of formation of magnesium chloride and oxide are comparable, reversible interconversion of these two materials is possible through the effects of the equilibrium(23)

$$MgO\,(\text{solid}) + Cl_2\,(\text{gas}) \rightleftarrows MgCl_2\,(\text{solid}) + \tfrac{1}{2}O_2\,(\text{gas}) \qquad (9)$$
$$\Delta F^\circ_{\text{reac }9} = \Delta F^\circ_{MgCl_2} - \Delta F^\circ_{MgO}$$
$$= \Delta F^\circ_{\text{reac }7} - \Delta F^\circ_{\text{reac }8}$$
$$= -RT \ln (p_{O_2}^{1/2}/p_{Cl_2})$$

---

(21) G F SMITH *Dehydration Studies Using Anhydrous Magnesium Perchlorate*, pp 22–32 G F Smith Chemical Co , Columbus, Ohio (1951)

(22) N V SIDGWICK *The Chemical Elements and Their Compounds*, vol 1 p 235 Oxford (1951)

(23) K K KELLEY *Energy Requirements and Equilibria in the Dehydration, Hydrolysis and Decomposition of Magnesium Chloride*, pp 18–20 Bureau of Mines Technical Paper 676, U S Government Printing Office, Washington, D C (1945)

Experimental studies have shown that the equilibrium represented by Equation (9) is achievable in practice.$^{(24,25)}$ Thus, it would appear that the composition of the vapour phase in contact with decomposing magnesium perchlorate and the rate of equilibration (Equation (9)) should primarily determine the nature of the reaction residue.

It is anticipated that if appropriate control of the gas ratio, $p_{O_2}^{1/2}/p_{Cl_2}$, could be maintained throughout a mass of decomposing magnesium perchlorate, the reaction product could be predetermined. Under the essentially irreversible conditions of the usual DTA or TGA experiment, it seems reasonable that the important factor will be the composition of the vapour phase in immediate contact with the pyrolysing material, i.e., the instantaneously evolved gaseous decompositions products. Below 427° ($\Delta F^\circ_{MgO,427} = \Delta F^\circ_{MgCl_2,427}$), breakdown of magnesium perchlorate by reaction (7) will yield an exceedingly oxygen-rich atmosphere which will then tend to convert the chloride to oxide by virtue of the reverse of reaction (9). The extent of conversion of chloride to oxide will be dependent on the rate of oxygen–chlorine exchange and the time duration of the oxygen gas evolution. As the oxygen issues from the interior of the decomposing magnesium perchlorate, the gas sweeps away chlorine which would tend to reconvert the oxide and provides the gaseous reactant partner for magnesium chloride. Thus, below 427°, the product distribution may be determined by the following reactions:

$$Mg(ClO_4)_2\,(\text{solid}) \rightarrow MgCl_2\,(\text{solid}) + 4O_2\,(\text{gas}), \tag{10}$$

and

$$MgCl_2\,(\text{solid}) + \tfrac{1}{2}O_2\,(\text{gas}) \rightarrow MgO\,(\text{solid}) + Cl_2\,(\text{gas}). \tag{11}$$

Above 427°, it appears that direct decomposition to magnesium oxide is possible, viz., $Mg(ClO_4)_2 \rightarrow MgO + Cl_2 + \tfrac{7}{2}O_2$.

It is of interest to note that decomposing anhydrous magnesium perchlorate does not liquefy even when heated to about 600°.$^{(11,12)}$ The DTA curve for anhydrous magnesium perchlorate reported by GORDON and CAMPBELL$^{(13)}$ must actually refer to magnesium perchlorate hexahydrate for both fusion and boiling phenomena are indicated by visual observations and by low temperature endotherms. A comparison of their DTA curve with those obtained for both the hydrated and anhydrous materials$^{(12)}$ shows a close resemblance to the curve for the hydrate.

The product distributions from magnesium perchlorate heated to about 600° in TGA experiments$^{(11)}$ are virtually uninfluenced by the gaseous atmosphere above the decomposing perchlorate, thereby indicating that the internal gaseous environment within the perchlorate determines the final pyrolysis products. TGA runs carried out in this laboratory in flowing argon and oxygen atmospheres gave, on the bases of chemical analyses, final residues of 93.4% MgO, 6.1% $MgCl_2$ and 0.5% $Mg(ClO_4)_2$ (by difference), and 93.5% MgO, 5.7% $MgCl_2$ and 0.8% $Mg(ClO_4)_2$ (by difference), respectively. Constant temperature studies (391° for 24 hr) show that the magnesium chloride produced can be maintained to some extent by removal of oxygen. Thus, under flowing argon, a residue of 16.2% $MgCl_2$, 5.3% MgO and 78.5% $Mg(ClO_4)_2$ (by difference) is obtained, whereas under flowing oxygen less magnesium chloride remains, i.e., 12.5% $MgCl_2$, 7.2% MgO and 80.3% $Mg(ClO_4)_2$ (by difference).

---

(24) F. HABER and F. FLEISCHMANN, *Z. Anorg. Chem.* **51**, 336 (1906).

(25) W. HIRSCHKIND, *Z. Anorg. Chem.* **67**, 113 (1909).

Internal oxygenation effects in decomposing perchlorates

Large local concentration and pressure inhomogeneities in the body of a mass of decomposing perchlorate can afford sufficient driving force to produce some oxide in the final residue of a perchlorate where the chloride is the otherwise favoured decomposition product. Thus the preparation of pure magnesium chloride from magnesium perchlorate appears to be impossible in the usual thermal decomposition reaction. This effect of internal oxygenation may account for the observed release of very small amounts of chlorine (parts per million in the oxygen evolved from potassium perchlorate(26)) and the resultant alkalinity due to the presence of some metal oxide (0.1–0.2% Li_2O from decomposed lithium perchlorate(10,27)) in the pyrolysis products from lithium, sodium,(11) calcium(12) and potassium perchlorates. Thus, the reaction below could be driven to the right by exceedingly high pressures of oxygen such as

$$2\mathrm{M}^{n}\mathrm{Cl}_{n} + \frac{n}{2}\mathrm{O}_2 \rightarrow \mathrm{M}_2^{n}\mathrm{O}_{n} + n\mathrm{Cl}_2 \qquad (12)$$

might occur during the decompositions of condensed phase perchlorate salts. Nevertheless the primary reaction routes for these perchlorates tend to give the corresponding chlorides. In the quantitative conversion of perchlorate salts to chlorides,(28,29) it is the usual practice to mix the solid perchlorate with a large quantity of anhydrous sodium carbonate and then to heat the mixture to fusion in a platinum crucible over a blast lamp. It seems likely in this procedure that any chlorine formed in the melt will then react with the sodium carbonate to reform chloride ions as per $Na_2CO_3 + Cl_2 \rightarrow 2NaCl + \frac{1}{2}O_2 + CO_2$. This reaction is essentially the reverse of Equation (12).

It is pertinent to note that the interaction of a gaseous pyrolysis product with a condensed phase reaction residue has also been reported to occur during the thermal decompositions of various metal oxalates.(30) In addition, the accumulation of high pressures of reaction gases within condensed phase residues has also been noted by a number of investigators.(31,32,33)

Enthalpy and entropy trends in metal perchlorate decompositions

The data in Table 1 demonstrate that whereas the enthalpy changes characterizing the alternate perchlorate decomposition states differ considerably, the corresponding entropy changes are quite similar. Therefore, the differences in free energy changes for reactions (3) and (4) reside primarily in the enthalpy changes. These latter are, in turn, related to the higher equivalent enthalpies of formation of the chlorides as compared with the oxides. The similarities in entropy changes between the two final states is not unexpected because almost the same number of gaseous molecules are produced in each reaction. Accordingly, an alternate means for predicting the course of perchlorate decompositions might be based on the relative equivalent heats of formation ($\Delta H^\circ_{\mathrm{equiv}} = \Delta H_{\mathrm{formation}}/n\nu$, n = valence of cation, and $\nu = 1$ for chloride and $\nu = 2$ for oxide) of the oxides and chlorides. This approach is less rigorous than that based on the free energy considerations. Nevertheless, the greater abundance of enthalpy of formation data in comparison to free energy of formation data makes this enthalpy development useful. Inspection of Table 2 [appropriate data collected from References (16) and (20)] indicates the ability of the equivalent enthalpy differences at 25° of the possible reaction product pairs to predict the final decomposition states. In general from Table 2, the effect of rising temperature on the differences in equivalent free energies of formation is small. It seems reasonable that over the limited temperature range considered here, a similar consistency will be shown by the differences in equivalent heats of formation of the oxides and chlorides.

---

(26) A. F. HARVEY, C. J. WASSINK, T. A. RODGERS and K. H. STERN, *Ann. New York Acad. Sci.* **79**, 971 (1960).

(27) M. M. MARKOWITZ and D. A. BORYTA, *J. Phys. Chem.* **65**, 1419 (1961).

(28) K. A. HOFMANN, A. METZLER and K. HOBOLD, *Ber. Chem. Dtsch. Ges.* **43**, 1080 (1910).

(29) F. D. SNELL and F. M. BIFFEN, *Commercial Methods of Analysis*, p. 128. McGraw-Hill, New York (1944).

(30) R. DAVID, *Bull. Soc. chim. France*, 719 (1960).

(31) G. GAFNER, *Trans. Faraday Soc.* **55**, 981 (1959).

(32) A. GLASNER and L. WEIDENFELD, *J. Amer. Chem. Soc.* **74**, 2467 (1952).

(33) A. GLASNER and M. STEINBERG, *J. Inorg. Nucl. Chem.* **16**, 279 (1961).

The rather close uniformity of thermodynamic values for reaction (3) as listed in Table 1 for the observed decompositions of the alkali metal perchlorates is noteworthy. The enthalpy changes for the decompositions following reaction (3) are small, thereby indicating that the free energy changes are favoured by the large entropy changes occasioned in these decompositions. This similarity in properties might indicate that lithium and sodium perchlorates also undergo an entropy change of about 88 e.u. upon decomposition to the chlorides. This then yields an estimated value of about −60 kcal/mole for the free energies of formation of lithium and sodium perchlorates.

Discussion

The metal perchlorates, like a number of other thermally unstable compounds (e.g., hydrogen peroxide, ethylene oxide, nitromethane, etc.) are thermodynamically stable with respect to their constituent elements but are unstable relative to certain other reaction products. The apparent stabilities of the pure metal perchlorates are probably due to the endothermic or usually small exothermic changes during decomposition so that self-propagating pyrolysis is not possible. It is likely that all metal perchlorates are irreversibly thermally unstable at moderate temperatures and that the limited upper range of decomposition temperatures merely reflects the intrinsic instability of the perchlorate group at a level where the decompositions can become kinetically measureable as with the DTA or TGA techniques.

The arguments presented thus far have referred solely to the relative stabilities of the possible final decomposition products as dictating the pyrolytic fate of a perchlorate. No consideration has been given the various kinetic steps by which the ultimate products are formed. The question arises, however, of the possibility of differences in product distributions between the hydrated and anhydrous forms of the same perchlorate due to kinetic steps involving hydrolysis of the perchlorate, decomposition of the perchloric acid so-formed and dehydration of the resultant metal hydroxide, i.e.,

$$M^{n+}(ClO_4)_n \cdot xH_2O \rightarrow M^{n+}(OH)_n + nHClO_4 + (x - n)H_2O$$

$$nHClO_4 \rightarrow \frac{n}{2}H_2O + \frac{n}{2}Cl_2 + 1.75nO_2$$

$$M^{n+}(OH)_n \rightarrow \tfrac{1}{2}M_2^{n+}O_n + \frac{n}{2}H_2O$$

$M^{n+}(ClO_4)_n \cdot xH_2O \rightarrow \tfrac{1}{2}M_2^{n+}O_n + \frac{n}{2}Cl_2 + 1.75nO_2 + xH_2O$ versus a kinetic sequence for the anhydrous perchlorate leading to the overall reaction $M^{n+}(ClO_4)_n \to M^{n+}Cl_n + 2nO_2$. However, those perchlorates susceptible to hydrolysis are probably the very ones which have chlorides more covalent than their oxides and thus the anhydrous perchlorates would be expected to decompose to oxides as well.

Dehydration of hydrated perchlorates is frequently quite difficult because of strong coordination of water molecules to the cation and extensive hydrogen bonding with the perchlorate anion.[34,35] As a result, in some instances dehydration and perchlorate decomposition reactions may occur simultaneously. The hydrolysis by water-vapour of a metal chloride is primarily dependent on the relative equivalent free energies of formation of the chloride and oxide. Thus, for the hydrolytic reaction

$$M^{n+}Cl_n + \frac{n}{2}H_2O\,(\text{gas}) \to nHCl\,(\text{gas}) + \tfrac{1}{2}M_2^{n+}O_n,$$

$$\Delta F^\circ_{\text{reac}} = (\tfrac{1}{2}\Delta F^\circ_{M_2^{n+}O_n} - \Delta F^\circ_{M^{n+}Cl_n}) + n(\Delta F^\circ_{HCl} - \tfrac{1}{2}\Delta F^\circ_{H_2O})$$

The magnitude of the term $(\Delta F^\circ_{HCl} - \frac{1}{2}\Delta F^\circ_{H_2O})$ is small at 25°C ($\simeq +4.5$ kcal) and decreases with increasing temperature. Within the range of perchlorate decomposition temperatures (400–600°), the value of this difference is very close to zero. Accordingly, the possible conversion of a chloride to oxide by hydrolysis appears remote except for those instances where the equivalent free energy differences of the reaction product pairs are small. The generality of the free energy criteria proposed for the original perchlorate decomposition reaction is thus preserved.

The preceding discussions have centred on the metal perchlorates. Nevertheless, the considerations presented here may be of value in rationalizing and predicting the thermal decomposition products of other metal halates such as chlorates, bromates, iodates and the like.

---

[34] A. F. Wells, *Structural Inorganic Chemistry* (2nd Ed.), pp. 441–443. Oxford (1950).

[35] N. V. Mani and S. Ramaseshan, *Z. Krist.* **115**, 97 (1961).

J Inorg Nucl Chem , 1963, Vol 25, pp 415 to 427 Pergamon Press Ltd Printed in Northern Ireland

MONONUCLEAR HYDROLYSIS OF TITANIUM (IV) FROM PARTITION EQUILIBRIA

A LIBERTI, V CHIANTELLA and F CORIGLIANO
Istituto di Chimica Analitica-Universita'-Napoli Italy

(*Received* 3 *August* 1962)

Abstract—The mononuclear hydrolysis constants of titanium (IV) have been calculated by means of partition data for titanium (IV) between aqueous solutions 0 1 M in perchlorate and organic solvents containing 8-hydroxyquinoline in chloroform and TTA in benzene The experimental data can be explained in terms of the following equilibria

$$[Ti(OH)_2^{2+}][H^+]/[TiOH^{3+}] \quad 10^{1\ 80}$$
$$[Ti(OH)_3^{+}][H^+]^2/[TiOH^{3+}] \quad 10^{1\ 20}$$
$$[Ti(OH)_4][H^+]^3/[TiOH^{3+}] \quad 10^{6\ 3}$$

Since the existence of Ti^{4+} is ruled out in the pH range 0 5 3, the solubility product of titanium (IV) hydroxide $[TiOH]^{3+}[OH^-]^3$ has been determined

The formation constants of the complexes titanium TTA and titanium oxine in water solutions have been calculated by taking into account hydrolytic equilibria

THE nature of the chemical species formed by titanium (IV) in solution is not well known, no systematic study of the equilibrium hydrolysis of this ion has been performed and different conclusions have been reached by different workers BARKSDALE(1) gives only speculative formulas for the various species, while BEUKENKAMP and HERRINGTON(2) claim as a result of an ion-exchange investigation that titanium (IV) exists in two ionic forms $Ti(OH)_3$ and $Ti(OH)_2^{2+}$, DELAFOSSE(3) however, from extraction studies, concludes that $Ti(OH)^3$ and TiO^{2+} exist together, the former predominating at pH 0 3 and the latter at pH 0 4

The present paper describes a study of distribution data for titanium(IV) between aqueous solutions and organic solvents containing various ligands Since the hydrogen ion concentration affects both the distribution equilibria and the titanium (IV) hydrolysis, when allowance is made for complexing by organic ligands in the aqueous phase, the distribution data can be used to calculate the constants of the hydrolytic equilibria A series of extractions of titanium solutions was carried out at constant ionic strength (0 1 M ClO^{4-}) at 25° with solvents containing 8-hydroxyquinoline (oxine) and thenoyltrifluoroacetone (TTA) over a wide range of concentration of the cation and of hydrogen ion The data are collected in Table 1 and log q is plotted versus pA⁻ for both systems in Figs 1 and 2, experimental details are reported elsewhere(4 5) The solid curves are based on values for the constants obtained by using the two parameter method of DYRSSEN and SILLEN(6) In the titanium oxine system the curve passing through most points has a slope which varies

---

(1) I BARKSDALE, *Titanium* Ronald Press, Co , New York (1949)

(2) J BEUKENKAMP and K D HERRINGTON, *J Amer Chem Soc* **82**, 3025 (1960)

(3) D DELAFOSSE **240,** 1991 (1955) *C R Acad Sci Paris*

(4) A LIBERTI and V CHIANTELLA, *Ann Chim* **52**, 495 (1962)

(5) A LIBERTI, V CHIANTELLA and F CORIGLIANO *Ann Chim* **52**, 813 (1962)

(6) D DYRSSEN and L G SILLEN, *Acta Chem Scand* **7**, 663 (1953)

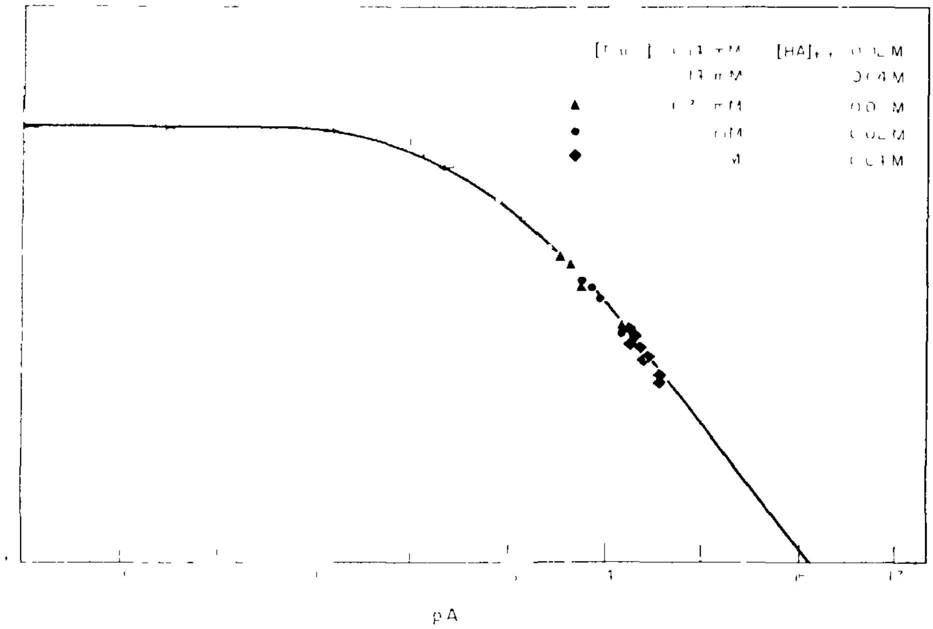


FIG. 1 Log (distribution ratio) vs pA (oximate ion)

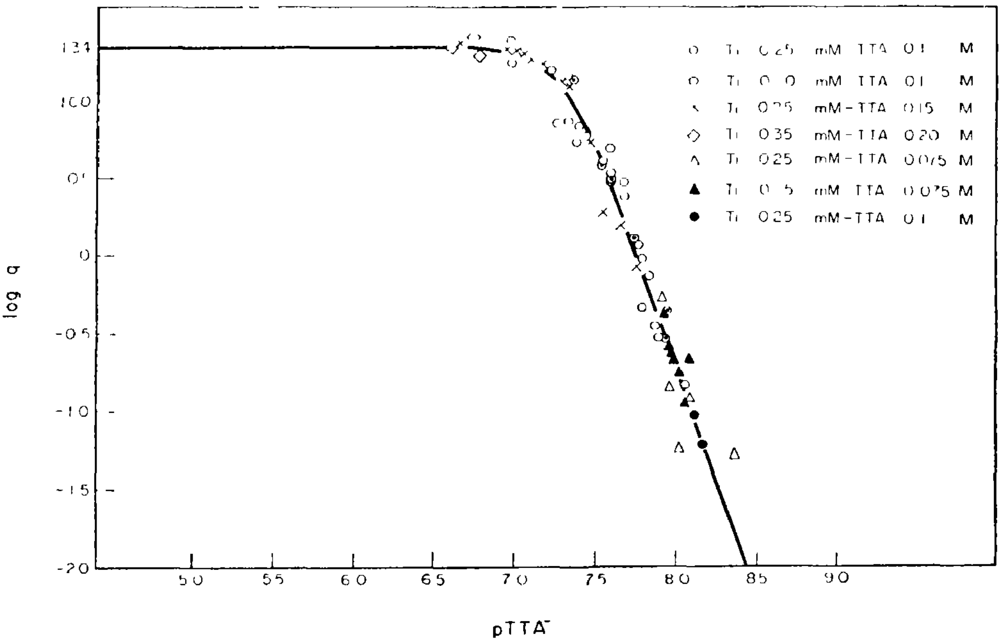


FIG. 2 Log (distribution ratio) vs pA (TTA)

from 0 to 2. For the system titanium TTA the curve has a slope between 0 and 3. It has been shown that the extracted complex is the only one present in the aqueous phase. The constants for these systems and for the titanium-salicylic acid complexes, obtained by the same procedure[(5)], are summarized in the following table.

Ligand	log (stability constant)				pH range	Number of ligands in the extracted species
Oxine HA	K_1	13.41	K_2	11.85	1.0-3.0	2
Salicylic acid H_2A	K_1	1.7	K_2	2.7	1.5-3.0	2
	K_3	3.7	K_4	4.7		
TTA	$K_{0,3}$	21.92			0.5-2.0	3

Since in the presence of a chelating agent the species extracted is the one which has no charge, and since the number of ligands per mole of titanium is 2,2 and 3 with oxine, salicylic acid and TTA respectively, it must be assumed from the principle of electroneutrality that titanium is present in different hydrolytic forms, and the extent of hydrolysis should be a function of the hydrogen ion concentration. The pH range in which titanium is extracted by TTA (presumably as $Ti(OH)(TTA)_3$) is slightly more acid (0.5-2.0) than that in which titanium forms complexes with other ligands (1.0-3.0). In more acid solution the hydrolysis equilibrium is displaced towards $Ti(OH)^{3+}$ and in less acid solution a more hydrolyzed species such as $Ti(OH)_2^{2+}$ takes part in the formation of the extracted complexes.

The experimental data of Table 1 have been used to calculate the hydrolysis equilibria by following the scheme, which accounts for the influence of a secondary ligand on the partition of an inner complex between an organic and an aqueous phase; in this case [OH⁻] has been taken as a secondary ligand. This scheme has been applied by several authors, e.g. Rossotti and Rossotti[(7)]. The equilibria are related to mononuclear hydrolysis of titanium, since in the range of concentration used, the experimental data do not indicate the existence of polynuclear hydroxo-complexes. The theoretical principles of the calculation are as follows.

The general expression for the distribution ratio q relative to the partition of a metal ion which undergoes hydrolysis, and which forms complexes which can be extracted by an organic solvent, is

$$q = \frac{\sum\limits_{B=0}\sum\limits_{N=1}[H_B MeA_N]_{org}}{\left\{[Me] + \sum\limits_{p=1} Me(OH)_p + \sum\limits_{b=0}\sum\limits_{n=1}[H_b MeA_n]\right\}}$$

$$q = \frac{\sum\limits_{B=0}\sum\limits_{N=1}\Lambda_{BN}x_{BN}h^{B}[A^-]^{N}}{1 + \sum\limits_{p=1} x_p h^{-p} + \sum\limits_{B=0}\sum\limits_{n=1} x_{b,n}h^{b}[A^-]^{n}}$$

where

$$\Lambda_{BN} = [H_B MeA_N]_{org}[H_B MeA_N]^{-1}$$

$$x_p = [Me(OH)p]h^{p}[Me]^{-1}$$

$$x_{b,n} = [H_b MeA_n][Me]^{-1}h^{-b}[A^-]^{-n}$$

---

(7) F. J. C. Rossotti and H. Rossotti, *Acta Chem. Scand.* **10**, 779 (1956).

$[A^-]$ is the concentration of the free ligand in aqueous solution and h the hydrogen ion concentration; b and B have negative values for complexes with OH groups. If the two phases have equal volumes, the sum of uncomplexed TTA in both phases, A, is given by

$$A = C_A - \sum_{b=0} \sum_{N=1} N[H_bMeA_N] - \sum_{b=0} \sum_{n=1} n[H_bMeA_n]$$

The last terms are negligible compared with C_A since with the experimental conditions usually employed $C_A \gg [Me]$. The concentration of A can be calculated from the following expression

$$C_A = [HA]_{org} + [HA] + [A^-] = [A^-]\{K_{HA}h(D+1)+1\} \tag{2}$$

where

$$K_{HA} = [HA]h^{-1}[A^-]^{-1} \quad \text{and} \quad D = [HA]_{org}[HA]^{-1}$$

If the acid is weak, $[A^-]$ can be neglected compared with other species and also $K_{HA}h(D+1) \gg 1$; from equation (2) we then have

$$[A^-] \simeq A\{K_{HA}h(D+1)\}^{-1}$$

Introducing this value in (1) we obtain

$$q = \frac{\sum\limits_{B=0} \sum\limits_{N=1} \Lambda_{BN} K_{BN} h^{B} A^{N}}{\left\{1 + \sum\limits_{p=1} x_p h^{-p} + \sum\limits_{b=0} \sum\limits_{n=1} K_{bn} h^{b-n} A^{n}\right\}} \tag{3}$$

where

$$K_{bn} = x_{bn} K_{HA}^{-n}(D+1)^{-n} \tag{3a}$$

We may assume that at high acidities titanium is not complexed by any organic ligand, and hence

$$\lim_{h \to \infty} (\partial \log q/\partial \log h)_{C_A} = \bar{B} - \bar{N} \tag{4a}$$

$$\lim_{h \to \infty} (\partial \log q/\partial \log C_A)_h = \bar{N} \tag{4b}$$

$\bar{B}$ and $\bar{N}$ are the average numbers of hydrogen ions and ligand groups attached to each metal ion in the complex in the organic phase. The values of $\bar{B} - \bar{N}$ and $\bar{N}$ allow us to obtain the stoichiometric coefficients of the extracted complexes. In absolute values $\bar{B} - \bar{N}$ is equal to the charge on the metal ion.

When $\bar{B} = 0$ and $\bar{N} = N$, i.e. only one complex is formed, we may define a function y as follows

$$y = \log q - N \log A + N \log h = \tag{5a}$$

$$= \log \Lambda_{0N} K_{0N} - \log \{1 + \sum_{p=1} x_p h^{-p} + \sum_{b=0} \sum_{n=1} K_{bn} h^{b-n} A^{n}\} \tag{5b}$$

From the plot of y vs. $(\log h)_{C_A}$ we obtain information on the nature of the species existing in aqueous solution. If the ligand is a weak base or acid, y is independent of log h and no complexes are formed; if y depends on log h only hydroxo complexes will be formed. If y depends on both log h and A we may either have formation of both hydroxo-complexes and organic ligand-complexes or of the latter only. In this

Table 1

Ti(IV)-oxine				Ti(IV)-TTA			
C_A (M)	$C_{Ti(IV)}$ (mM)	log q	pA^-	C_A (M)	$C_{Ti(IV)}$ (mM)	log q	pA
0 040	0 140	0 551	12 364	0 200	0 250	1 294	6 757
0 040	0 140	0 926	11 940	0 200	0 250	1 405	6 737
0 040	0 140	0 680	12 162	0 200	0 250	1 348	6 602
0 040	0 140	1 226	11 774	0 154	0 250	1 269	6 647
0 040	0 140	1 226	11 593	0 150	0 250	1 091	7 328
0 040	0 140	0 867	9 104	0 150	0 250	1 137	7 296
0 040	0 140	0 916	11 120	0 150	0 250	1 239	7 170
0 040	0 140	0 237	13 189	0 150	0 250	1 298	7 046
0 040	0 140	1 076	10 845	0 150	0 250	1 319	7 009
0 040	0 140	0 197	12 382	0 150	0 250	1 335	6 952
0 040	0 140	1 408	10 588	0 150	0 250	0 843	7 259
0 040	0 140	0 865	10 000	0 150	0 250	0 080	7 767
0 040	0 140	1 097	9 389	0 150	0 250	0 202	7 676
0 040	0 140	0 957	9 455	0 150	0 250	0 671	7 552
0 040	5 000	2 397	14 376	0 150	0 250	0 727	7 466
0 040	5 000	2 885	14 576	0 150	0 250	1 251	7 093
0 040	5 000	3 000	14 574	0 075	0 250	0 271	7 991
0 040	5 000	- 2 584	14 440	0 075	0 250	0 856	7 967
0 040	5 000	2 328	14 300	0 075	0 250	1 244	8 024
0 040	5 000	2 657	14 360	0 075	0 250	0 921	8 082
0 040	5 000	2 178	14 250	0 075	0 250	1 283	8 372
0 040	5 000	2 205	14 150	0 100	0 250	0 536	7 901
0 040	5 000	2 355	14 260	0 100	0 250	- 0 251	7 600
0 040	5 000	2 657	14 390	0 100	0 250	0 889	7 219
0 020	0 140	0 895	13 410	0 100	0 250	1 190	7 219
0 020	0 140	0 420	13 110	0 100	0 250	0 311	7 800
0 020	0 140	0 127	12 880	0 100	0 250	0 385	7 686
0 020	0 140	0 688	11 190	0 100	0 250	0 726	7 393
0 020	0 140	0 281	12 283	0 100	0 250	0 533	7 938
0 020	0 140	0 001	12 555	0 100	0 250	- 0 033	7 800
0 020	0 140	0 827	11 228	0 100	0 250	0 684	7 600
0 020	0 140	0 384	11 917	0 100	0 250	- 0 358	7 938
0 020	0 140	0 890	11 618	0 100	0 250	0 100	7 748
0 020	0 140	1 026	11 206	0 100	0 250	0 499	7 595
0 020	0 140	0 688	10 904	0 100	0 250	0 764	7 454
0 020	1 000	2 220	14 160	0 100	0 250	0 486	7 595
0 020	1 000	1 691	13 940	0 100	0 250	0 843	7 259
0 020	1 000	1 550	13 850	0 100	0 200	0 137	7 841
0 020	1 000	1 454	13 760	0 100	0 200	0 072	7 767
0 020	0 300	1 548	13 760	0 100	0 200	0 575	7 535
0 020	0 300	- 1 137	13 690	0 100	0 200	0 836	7 412
0 020	0 300	0 974	13 560	0 100	0 200	0 859	7 344
0 020	0 300	2 183	14 162	0 100	0 200	1 239	6 981
				0 100	0 250	1 159	7 327
				0 100	0 250	1 142	7 362
				0 100	0 250	0 606	7 546
				0 100	0 250	0 565	7 867
				0 075	0 250	0 366	7 911
				0 075	0 250	0 616	7 967
				0 075	0 250	0 752	8 024
				0 075	0 250	0 677	8 082
				0 075	0 250	0 598	7 962
				0 075	0 250	0 675	7 984
				0 075	0 250	0 941	8 062
				0 100	0 250	0 838	8 064
				0 100	0 250	- 1 040	8 115
				0 100	0 250	1 218	8 172

case in order to obtain x_p and $X_0 \times K_0 \times y$ is extrapolated to zero ligand concentration to obtain the function y^0

$$y_0 = \log X_0 \times K_0 \times \quad \log\{1 + \sum_{p=1} x_p h^{-p}\} \tag{6}$$

From a plot of this function versus log h the hydrolysis constants may be calculated

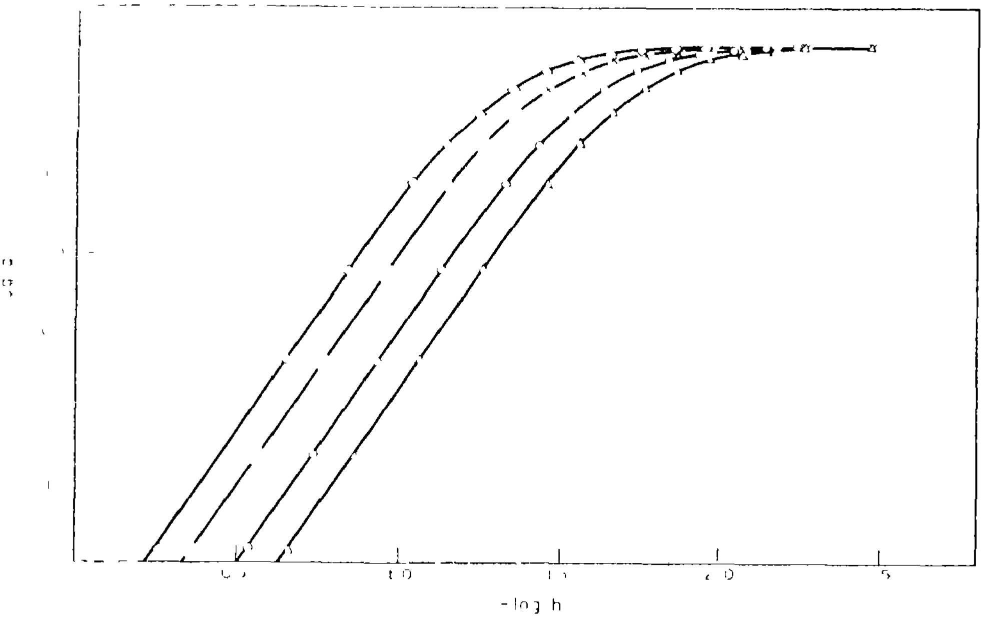


FIG. 3 Titanium-TTA log q vs log h for various ligand concentrations

This procedure has been applied to the experimental data of Table 1, in order to reduce the error in the calculation and to have a larger number of values, points have been taken from the curve drawn through the experimental values

Titanium (IV) TTA system

In Fig 3 the logarithm of the distribution ratio is plotted versus log h for various ligand concentrations (0.075, 0.1, 0.15, 0.2 M), from the slope, according to (4a),

TABLE 2

log q	pH (C_A 0.075)	pH (C_A 0.100)	pH (C_A 0.150)	pH (C_A 0.200)	y	y_0		log h
0.70	1.159	0.934	0.763	0.650	0.502	2.85	0.05	2.9
0.12	1.259	1.134	0.963	0.850	−0.522	2.58	0.06	2.8
0.44	1.459	1.334	1.163	1.050	0.562	−2.31	0.05	−2.7
0.71	1.559	1.434	1.263	1.150	0.610	2.02	0.05	−2.6
0.90	1.659	1.534	1.363	1.250	0.702	1.79	0.07	−2.5
1.07	1.759	1.634	1.463	1.350	0.832	−1.54	0.06	2.4
1.18	1.859	1.734	1.563	1.450	−1.022	1.38 ±	0.06	−2.3
1.26	1.959	1.834	1.663	1.550	1.247	−1.21	0.05	−2.2
1.29	2.059	1.934	1.763	1.650	1.512	1.02	0.06	−2.1
1.32	2.159	2.034	1.863	1.750	−1.782	0.81	0.14	−2.0
1.33	2.259	2.134	1.963	1.850	−2.072			

the value $\bar{B} - \bar{N}$ is obtained as 3 By interpolation a series of values of log q/log C_A at constant hydrogen ion concentration is obtained the slope of these lines yields N 3 We have therefore $\bar{B} = 0$ and since $\bar{B} - \bar{N}$ is the charge on the metal ion, its formula, neglecting hydration, should be $TiOH^{3+}$ The values of y (Table 2) calculated from equation (5a) are plotted vs $(\log h)_{C_A}$ in Fig 4 the graph shows that for h 0 1 y is constant (0 5) and independent of log h, but at lower acidity separate lines are obtained for different concentrations of ligand because of the formation of complexes in the aqueous phase By interpolation values of y C are obtained at constant hydrogen ion concentration, through these points smooth curves were drawn to obtain by extrapolation values corresponding to $C_t = 0$ (Fig 5) Some difficulty has been experienced in obtaining this value, values of y_0 in Table 2 represent the average between the two extreme values (dotted lines obtained by extrapolation) From the plot of y_0 versus log h it is possible to calculate the unkowns in equation (6), viz

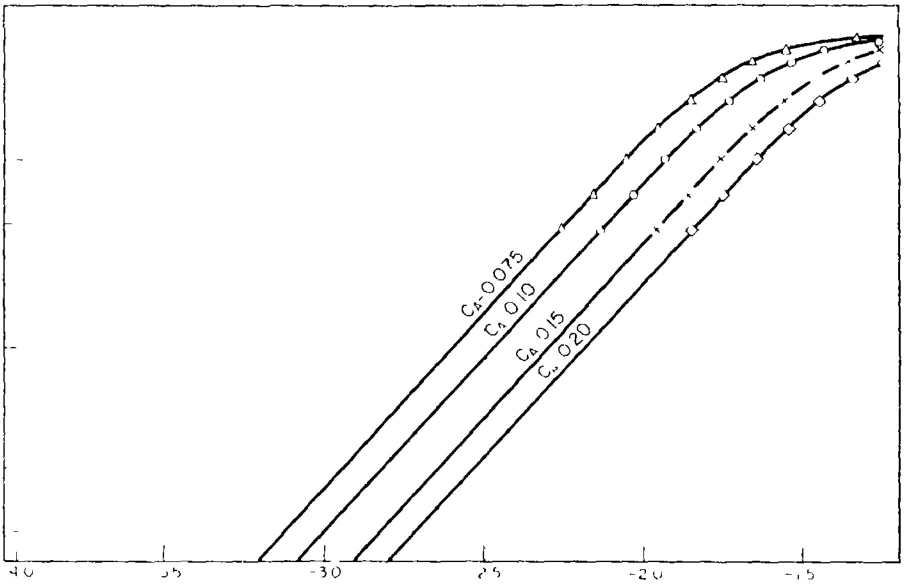


FIG 4 —Titanium–TTA y (equation 5) vs $(\log h)_{C_t}$

$$y_0 - \log \Lambda_{0\,3}K_{0\,3} \quad \log\left(1 \quad \sum_{p\,-1} x_p h^{\,p}\right) \tag{7}$$

This can be done graphically as suggested by SILLEN(8), by superimposing on the points of the graph of y_0 versus log h (a-Fig 6) a family of theoretical curves of the type $Y(X)t$ The best fit was obtained with a curve employing three constants and setting t - 2 The normalized variables X and Y are given by

$$Y - y_0 - \Lambda_{0\,3}K_{0\,3} = -\log\left(1 + t\,10^{X} + 10^{2X} \quad 10^{3X}\right)$$

$$X - \log h \quad \tfrac{1}{3}\log x_3$$

---

(8) L G SILLEN, *Acta Chem Scand* **10**, 186 (1956)

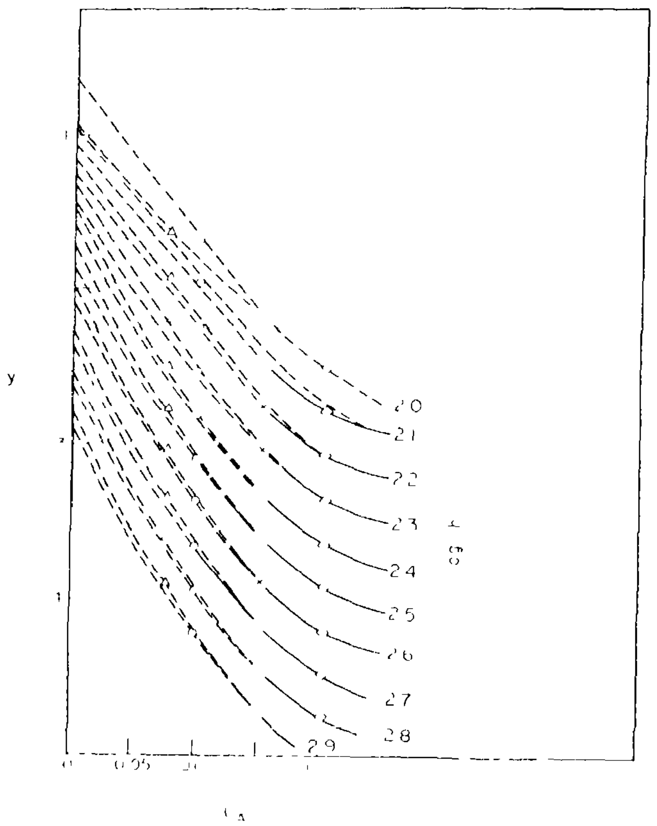


FIG. 5. Titanium TTA. Calculation of y_0 (Equation 7)

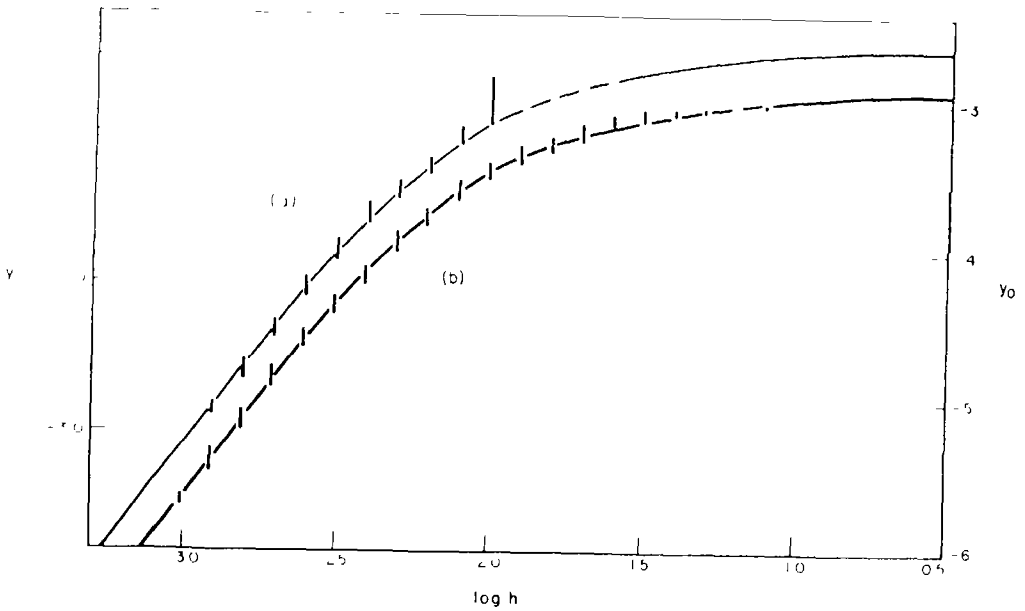


FIG. 6.—Graphic determination of the constants. Values of y_0 (vertical lines) versus log *h*. curve *A* titanium-TTA, curve *B* titanium-oxine. The full curve is calculated for $t = 2$

where

$$t = x_1 x_3^{-1/3} - 2$$

and (8)

$$10^{\,3s} = x_3 h^{\,3}$$

The equation with the normalized variables is equivalent to equation (7) The following values have been obtained

$\log x_1 = 1\ 809$ $\quad\log x_2 \ -\ 4\ 22$ $\quad\log x_3 = -6\ 33$

$\Lambda_{0\,3}K_{0\,3}$ $\quad 0{\cdot}45 \pm 0\ 05$

Titanium–8 hydroxyquinoline

The experimental data (Table 1) have been treated similarly, allowing for the different nature of the ligand, which behaves as a dibasic acid The ligand concentration may be calculated from the equation

$$[A\ ] \quad K_1K_2h^{\,2}[H_2A^{+}]$$

where K_1 and K_2 are the ionization constants of H_2A^{+}, for high values of h, $[H_2A^{+}]$ is approximately equal to the total ligand concentration A The limiting slope of the plot of $\log q$ versus $(\log h)_{C_A}$ is

$$\lim_{h \to \infty} \{\partial \log q / \partial \log h_{C_A}\} \ - \bar{B} - 2\bar{N}$$

and hence is equal to -4, and that of the plot of $\log q$ versus $(\log C_A)_h$ according to equation (4b) is equal to 2 Consequently $\bar{B}$ 0 and $\bar{N}$ 2, so that the extracted species, ignoring hydration, should be $Ti(OH)_2A_2$ This complex is therefore formed from $Ti(OH)_2^{2+}$, which seems to preferentially bind oxine For this system ν (equation 5) is given by

$$\nu = \log q - 2\log A + 4\log h$$

$$- \log \Lambda_{0\,2}K_{0\,2} \quad \log\Big(1 + x_p h^{-p} + \sum_{b\ 0} \sum_{n\ 1} K_{b\,n} h^{b-2n} A^{n}\Big)$$

TABLE 3

	C_A 0 04		C_A 0 02		C_A 0 01		C_A 0 005				
log q	pH	ν	pH	ν	pH	ν	pH	ν	ν_0		pH
5 685	0 030	3 009	0 180	3 007	0 331	3 007	0 481	3 007	5 67	0 03	3 0
4 687	0 280	3 011	0 430	3 009	0 581	3 009	0 748	3 009	5 40	0 04	2 9
3 696	0 530	3 020	0 680	3 018	0 831	3 018	0 981	3 018	5 12	- 0 05	2 8
3 106	0 680	3 030	0 830	3 028	0 980	3 028	1 131	3 028	4 85	0 05	2 7
2 337	0 880	- 3 061	1 030	3 059	1 181	3 059	1 331	3 059	4 60	0 04	2 6
1 784	1 030	3 110	1 180	3 106	1 331	3 106	1 481	3 106	4 35	0 05	2 5
1 266	1 179	3 188	1 330	3 188	1 481	3 188	1 631	3 188	4 15	0 05	2 4
0 653	1 380	3 379	1 530	3 375	1 681	3 375	1 831	3 375	3 92	0 06	2 3
0 259	1 530	3 585	1 680	3 581	1 831	3 581	1 981	3 581	3 76	0 05	2 2
0 079	1 680	3 847	1 830	3 843	1 981	3 843	2 131	3 843	3 59	0 04	2 1
0 448	1 880	4 278	2 030	4 274	2 181	4 274	2 331	4 274	3 47	0 04	2 0
0 661	2 030	4 665	2 180	4 661	2 331	4 661	2 461	4 581	3 35	0 03	1 9
0 830	2 296	5 560	2 443	5 544	2 558	5 402	2 685	5 308	3 26	0 03	1 8
1 000	2 758	-7 238	2 858	7 034	3 000	7 000	3 059	6 634	3 19	0 03	1 7
1 044	3 378	9 674	3 378	-9 070	3 479	8 872	3 481	8 278	3 12	0 03	1 6
1 049	4 000	12 157	4 000	11 53	4 000	10 959	4 000	10 349	3 08	0 03	1 5
									3 06	0 02	1 4
									3 04		1 3

As in the preceding case the values of x in Table 3 have been plotted versus C_A at constant hydrogen ion concentration, and by extrapolation to C_A 0, values of y_0 (Table 3) have been graphically obtained Points corresponding to y_0 vs log h are plotted (b-Fig 6) and a family of theoretical curves $Y(X)_t$ has been superimposed as in equation (8), the best fit is again obtained using three constants and setting $t = 2$ The following values have been obtained

$$\log x_1 \quad 1\ 794 \quad \log x_2 \quad 4\ 19 \quad \log x_3 \quad 6\ 285 \quad \log X_{0\,2}K_{0\,2} \quad 2\ 90$$

The values of x are in good agreement with those obtained for the titanium TTA system The constants relative to hydrolysis equilibria of titanium(IV) obtained by the two methods are expressed as average values in Table 4 A more refined treatment was carried out based on equation (5b), when the following function is obtained

$$J \quad X_{0x} K_{0x} 10^{y} \{1 + x_1 h^{1} + x_2 h^{2} + x_3 h^{3}\} \quad \sum_{b\;0} \sum_{n\;1} K_{b\,n} h^{b\;n} A^{n} \tag{9}$$

TABLE 4

System	$\frac{[Ti(OH)_2^{2+}][H^+]}{[TiOH^{3+}]}$	$\frac{[Ti(OH)_3^{+}][H^+]^2}{[TiOH^{3+}]}$	$\frac{[Ti(OH)_4][H^+]^3}{[TiOH^{3+}]}$
	log x_1	log x_2	log x_3
Ti(IV) OH TTA	1 809	4 22	6 330
Ti(IV) OH oxine	1 794	4 19	6 285
Average values	1 80	4 20	6 31

By plotting log J versus log Ah^{1} for the titanium TTA system a straight line is obtained of slope 3 0 the intercept for log Ah^{1} 0 (Fig 7*B*) yields log $K_{0\,3}$ 1 86 and therefore $X_{0\,3}$ 1 41 $\pm$ 0 05 By replacing the former value log $K_{0\,3}$ 6 38 and D 40 in equation (3a) a more accurate value for the formation constant of the titanium(IV) TTA complex is obtained

$$\log x_{0\,3} \quad 22\ 12$$

For the titanium oxine system the points of the log J vs log Ah^{2} lie on two straight lines, one in the range 0 50 M log Ah^{2} 2 5 M, has a slope equal to 1 and the other, in the range log Ah^{2} 2 5 M has a slope equal to 2 By extrapolation of these two lines to log Ah^{2} 0 we obtain for the former range log $K_{0\,1}$ 1 13 and for the latter log $K_{0\,2}$ -3 95, log $X_{0\,2}$ is therefore equal to 1 05 By using these values a more accurate value for the stepwise constants can be calculated from the equation

$$x_{b\,n} \quad K_1^{n} K_2^{n} K_{b\,n}$$

By substituting

$$\log x_{0\,1} = 13\ 53 \qquad \log x_{0\,2} = 25\ 37$$

These calculations show that hydrolytic equilibria have a minor effect upon the formation constants of these complexes

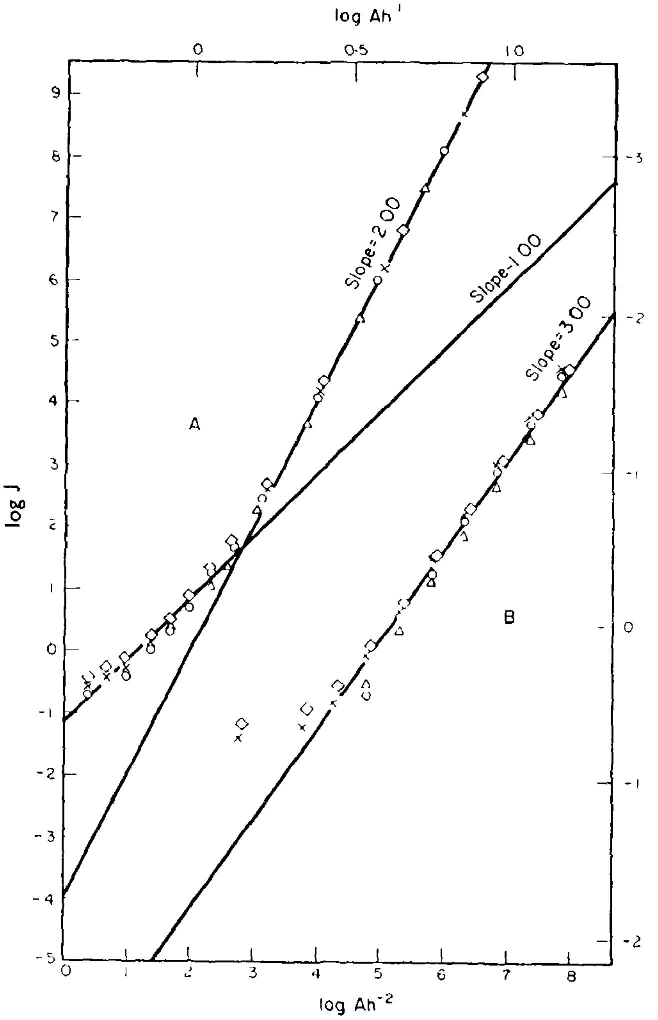


Fig. 7. –Log J (equation 9) versus log Ah^{-2} (A titanium-oxine) and versus log Ah^{-1} (B titanium-TTA)

The solubility product of titanium hydroxide

A rough estimate of the solubility product of titanium (IV) hydroxide has been made by Latimer,(9) who calculated from free energy values

$$TiO(OH)_2 \rightleftharpoons TiO^{2+} + 2OH^-, \qquad K \simeq 10^{-29}$$

Wilson and Wilson(10) reported for the same reaction $K = 6.3 \times 10^{-49}$. In order to measure the solubility product of titanium hydroxide, acid solutions of titanium (IV) perchlorate have been added to sodium carbonate; the pH range was 1–2 and the titanium (IV) concentration about 10^{-4} M. The solutions were left for about

---

(9) W. M. Latimer, *Oxidation Potentials*, Prentice-Hall, New York (1953).

(10) C. L. Wilson and D. W. Wilson, *Comprehensive Analytical Chemistry*, Vol. 1A. Elsevier, Amsterdam (1961).

20 days in order to attain equilibrium. The hydrogen ion concentration was measured and the dissolved titanium determined spectrophotometrically after extraction with hydroxyquinoline. The following are typical results:

$\mathrm{Ti}_{(\mathrm{anal})}$	$\mathrm{Ti}_{(\mathrm{equil})}$	pH
log Ti	log Ti	
3.602	3.776	1.856
3.602	4.817	2.192
3.602	5.097	2.401

At lower pH values no precipitate was formed. By expressing the equilibrium titanium (IV) concentration as $\mathrm{Ti(OH)}_x^{(4-x)+}$, since no experimental evidence for Ti^{4+} was found, the solubility product is given by

$$K_s = [\mathrm{Ti(OH)}_x]^{(4-n)+}[\mathrm{OH}^-]^n \quad \text{where } x = 4-n \tag{10}$$

For two pairs of experimental values we have

$$pK_s = p\mathrm{Ti}_1 + np\mathrm{OH}_1 \quad \text{and} \quad pK_s = p\mathrm{Ti}_2 + np\mathrm{OH}_2$$

By using $pK_w = 13.77$ and solving

$$n = 3 \qquad x = 1$$

Substituting in (10) we have therefore, averaging the results,

$$[\mathrm{TiOH}^{3+}][\mathrm{OH}^-]^3 = 10^{9.34}$$

According to the results of this study, this expression should be considered the more correct formulation for the solubility product of titanium hydroxide.

DISCUSSION

The use of partition data for titanium between aqueous solutions and organic solvents containing various ligands to calculate the hydrolysis equilibria of titanium (IV) shows that the experimental data can be explained by means of three constants. It can be assumed with a high degree of probability that Ti^{4+} does not exist in solution and that TiOH^{3+} is the less hydrolysed species present at moderate high acidity. This assumption is supported by theoretical and experimental considerations. On account of its electronic structure, and by comparison with other ions of Group IVA the possibility of the existence of an elementary ion Me^{4+} decreases from hafnium to titanium with decreasing ionic radius. The ionic radius of Ti^{4+} is very small (0.68 Å) and this ion may acquire an appreciable fraction of the electron density of an oxygen donor by forming a strong covalent bond. Ion exchange studies have shown[11] that at a pH lower than 1 and in the presence of perchlorate, titanium forms complexes: as a consequence any experimental measurement of the first hydrolysis step is prevented and the existence in solution of Ti^{4+} is ruled out.

The equilibrium constants for titanium (IV) hydrolysis are collected in Table 5 and the distribution of various hydrolytic species as a function of hydrogen ion concentration is presented in Fig. 8. These constants refer to mononuclear hydrolysis, since in the concentration range investigated no polynuclear complexes could

---

[11] A. LIBERTI and M. VICEDOMINI, In press.

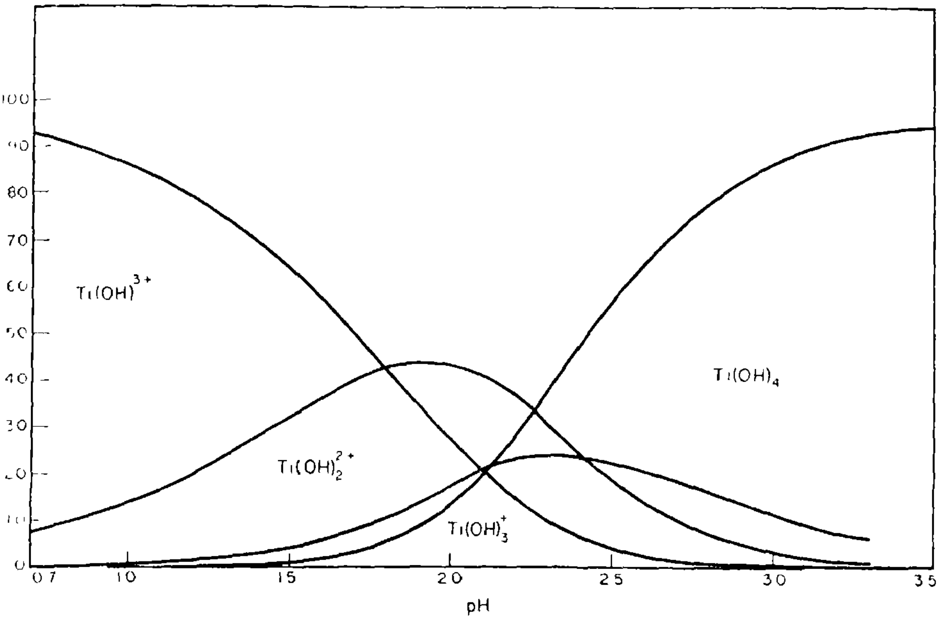


FIG 8 —Distribution of titanium-OH species versus log h

be detected the conclusions of this research are therefore restricted to very dilute solutions (< 10^{-4} M), and to pH 1–3 The addition of any ligand to a titanium (IV) solution causes the formation of a complex in which the number of hydroxyl ions depends on the hydrogen ion concentration of the solution and on the specific nature of the ligand The existence in aqueous solution of complexes containing unhydrolysed titanium ion seems unlikely The difficulty of obtaining accurate distribution measurements and the introduction of unknown parameters associated with the extracting reagent render the partition method not the most suitable for a quantitative investigation of the hydrolysis of metal ions The accuracy of the numerical values is also decreased by the numerous extrapolations involved in the calculation In spite of these limitations the good agreement between the results obtained from experimental distribution data for two different ligands indicate confidence in the reported values

J Inorg Nucl Chem , 1963, Vol 25, pp 429 to 439 Pergamon Press Ltd Printed in Northern Ireland

COUNTERCURRENT EXTRACTION OF THE RARE-EARTH ACETYLACETONATES*

W B Brown,† G W Pope,‡ J F Steinbach and W F Wagner
Department of Chemistry, University of Kentucky, Lexington, Kentucky

(*Received* 5 *July* 1962)

Abstract—The countercurrent distribution behaviour of the rare-earth acetylacetonates in different solvent systems has been studied Solubilities of the chelates in various solvents were determined in order to obtain data on the partition coefficients The hydrated rare-earth acetylacetonates hydrolyze upon dissolving in benzene Excess acetylacetone prevents hydrolysis and lowers the solubility of the chelates in the organic phase A four-component system using acetylacetone, chloroform, methanol and water was developed The acetylacetone in the chloroform phase suppressed hydrolysis and the methanol in the aqueous phase increased the solubilities of the chelates by a factor of ten over the solubilities in the water–acetylacetone system

The theory of the extraction of metal chelates has been developed by Kolthoff and Sandell,[1] Irving and Williams,[2] and more recently by Rydberg[3] who has derived equations relating the distribution coefficient to the formation constants of the chelate, pH, partition coefficients of the chelate and reagent, and dissociation constant of the reagent Rydberg postulated complexes of the general form $M_mR_n(OH)_p(HR)_r(Org)_s(H_2O)_t$ The exact composition of the complex could be determined only in special cases, but the concept of the general composite extractable species may serve as a useful guide in further studies Owing to the many discrepancies in the literature describing the properties of the rare-earth acetylacetonates, it was necessary to examine more thoroughly the characteristics of the compounds, a study which has been reported in a previous article[4] Because of the tendency of the rare-earth acetylacetonates to hydrolyse, polymerize, and form solvates with water and some organic solvents, a study of their extraction might be illustrative of the behaviour of the Rydberg-type complex

If countercurrent extraction is carried out at a sufficiently high pH for the complete formation of the chelate, a knowledge of the partition coefficient of the chelate is of paramount importance A reasonably good estimate of the partition coefficient can be obtained from the solubility of the chelate in each of the two phases This paper reports a study of the solubilities of the rare-earth acetylacetonates in several solvents, and the countercurrent extraction of some of the rare-earths in systems developed from the solubility and extraction data

---

* From dissertations submitted by W B Brown and G W Pope to the Graduate School of the University of Kentucky in partial fulfillment of the requirements for the degree of Doctor of Philosophy and presented in part before the Analytical Division of the 138th National Meeting of the American Chemical Society at New York City September, 1960

† Present address Monsanto Chemical Co , Miamisburg, Ohio

‡ Present address International Business Machines, Lexington, Ky

I M Kolthoff and E B Sandell, *J Amer Chem Soc* **63,** 1906 (1941)

H M Irving and R J F Williams, *J Chem Soc* 1841 (1949)

J Rydberg, *Arkiv Kemi* **8,** 101 (1955)

G W Pope, J F Steinbach and W F Wagner, *J Inorg Nucl Chem* **20,** 304 (1961)

EXPERIMENTAL

Reagents. Rare-earth oxides 99.9 per cent purity, were obtained from Michigan Chemical Company and Lindsay Chemical Company. Acetylacetone obtained commercially was extracted once with 10 per cent ammonia, washed twice with water and distilled through a 40 cm column packed with glass helices. The fraction boiling between 138 and 139.5° at 740 mm was used. All other reagents met American Chemical Society specifications or were of the highest grade available commercially.

Preparation of chelates. The method of Stites *et al.*[5] was used. The trihydrated, monohydrated, and monobasic rare-earth acetylacetonates were prepared as described in the previous article.[1]

Apparatus. A Beckman Model DK-2 recording spectrophotometer was used for all spectrophotometric measurements.

A Beckman Model G pH meter was employed for all pH measurements and potentiometric measurements. A J-type mercury electrode served as the indicator electrode in the potentiometric titrations.

A Craig countercurrent apparatus consisting of thirty tubes was used for all countercurrent extractions.

A Norelco X-ray Diffractometer was used for all X-ray diffraction powder patterns.

An Applied Research Laboratories 1.5 metre grating spectrograph, Model 6200, was used for the analysis of samples from some of the distribution studies.

Solubility studies. A well-stirred water bath, maintained at 30 ± 0.1°, was used for all determinations. Samples of the chelate and solvent were placed in 25 ml or 50 ml volumetric flasks. Several glass beads were added to the flask to increase the agitation. Each chelate solvent sample was prepared in duplicate. One flask of each pair was heated to 40–45° in a water-bath and then placed in the thermostatted bath. The other flask of the pair was placed directly into the constant-temperature bath without heating. The flasks in the bath were shaken occasionally during a three to five day period, after which samples were taken for analysis. Samples of 5 ml were taken from the 25 ml flasks and 10 ml from the 50 ml flasks and pipetted into previously ignited and weighed crucibles. A few drops of dilute nitric acid were added and the solution was evaporated on a warm hot plate under heat lamps to prevent bumping. When the solvent had evaporated, the crucibles were placed in a muffle furnace and heated to 900° for 1 hr, cooled and placed in a desiccator containing a desiccant and an absorbent for carbon dioxide. The crucibles were weighed, and reheated to constant weight. From the weight of the rare-earth oxide, the solubility was calculated. Check analyses on some samples were made by titration with EDTA using PAN indicator and a standard zinc solution as a back-titrant.[6] After two or three additional days in the constant-temperature bath another sample was taken and analysed to confirm that equilibrium had been attained.

Countercurrent separations. Several different solvent systems were used in the countercurrent extractions of which some contained a buffered aqueous phase. In each case, the organic and

TABLE 1 — OPERATING CONDITIONS FOR SPECTROGRAPHIC ANALYSIS

Excitation	D.C. Spark, 250 V at 3.2 As from Applied Research Laboratories Model 5700 Multisource Unit Interrupted discharge Continuous initiation Resistance—25 Ω Capacitance—60 microfarad Inductance—none (130 millihenry residual)
Electrodes	1¼ in by ¼ in copper electrodes
Analytical gap	2 mm
Slit width	20 μ
Slit filter	None
Exposure	20 sec, no presparking
Region	3300 to 4600 Å in second order
Film	Kodak Spectrum Analysis No. 1
Calibration of Film	Two-step filter method
Film Processing	Developed for 2½ min at 21°C in Eastman Kodak D-19, fixed for 5 min, washed for 15 min
Densitometry	Applied Research Laboratories Comparator-Densitometer

---

[5] J. G. Stites, C. N. McCarty and L. L. Quill, *J. Am. Chem. Soc.* **70**, 3142 (1948).

[6] K. L. Cheng, *Chemist Analyst*, **47**, 94 (1958).

aqueous phases were prepared and allowed to come to equilibrium with each other before being placed in the apparatus. The solution of the chelates was placed in tube number zero in the Craig extraction apparatus. Ten ml of the lower phase was added to each of the other tubes of the apparatus. During the extraction process, the phases were equilibrated for 5 min, allowed to separate for 1 min, and the upper phase then transferred. After thirty transfers, the tubes were emptied into 30 ml bottles and the phases were sampled and analysed by one or more of the analytical methods described in the next paragraph. Curves, showing the amount of each rare-earth present in the individual tubes, were prepared from the results of the analyses.

Analytical procedures. Spectrophotometric determinations were made for erbium at 377 mμ, holmium at 450 mμ and neodymium at 580 mμ. The residue obtained by evaporating the solutions from each tube of the Craig apparatus was dissolved in 3 ml of a 10 per cent solution of acetylacetone in methanol. This solution was placed in a 1 cm square Corex cell and scanned over the range of 600 to 360 mμ. The concentration of each rare earth was obtained from the corresponding Beer's Law plot.

Spectrographic analyses were made by dissolving the residue from each extraction tube in 5 ml of dilute hydrochloric acid, and evaporating 0.02 ml of this solution on a ¼ in copper electrode. The spectrographic analysis was then made using the conditions listed in Table 1. The transmittance of the chosen line was read from the film and converted to relative intensity from a calibration chart. The wavelengths of the lines used for each element are given in Table 2. In some cases semi-quantitative data were used by plotting the densities of the analysis lines against the tube numbers.

TABLE 2. WAVELENGTHS OF LINES SELECTED FOR SPECTROGRAPHIC ANALYSIS

Element	Wavelength (Å)
Dysprosium	3531.7 4000.5
Erbium	3906.3
Gadolinium	3422.4
Holmium	3748.2
Neodymium	3951.1
Samarium	4424.3
Terbium	3509.2
Ytterbium	3988.0
Yttrium	3774.3

RESULTS AND DISCUSSION

The solubility of nine rare-earth acetylacetonates in various organic solvents at 30 C is shown in Table 3. All the solvents except as noted in the table were saturated

TABLE 3.—SOLUBILITIES OF THE RARE EARTH ACETYLACETONATES AT 30 C (in mmoles per litre)

Solvent	Pr	Nd	Sm	Gd	Dy	Ho	Er	Yb	Y
Water, buffered at pH 6.0	2.4	2.4	2.5	2.7	3.2	3.3	5.4	3.2	5.1
Water plus 2 mole % HAcac	4.1	4.2	4.5	5.0	6.4	7.4	8.3	16	7.1
Benzene, anhydrous	12	14	22	32	65	98	128	225	91
Benzene	7.5	10	12	14	40	55	75	220	40
Benzene-HAcac, 0.8 0.2 m f	0.6	0.5	0.5	0.8	1.9	3.9	8.0	40	3.5
Benzene-HAcac, 0.5 0.5 m f	0.9	0.7	1.3	1.1	5.2	8.7	19	70	9.6
Benzene-HAcac, 0.2 0.8 m f	1.5	1.4	1.6	1.4	4.6	7.1	16	90	9.4
Acetylacetone	3.2	3.0	3.4	3.1	7.4	11	22	113	12
Carbon tetrachloride	3.2	3.5	6.6	7.5	16	26	37	112	19
n-Hexanol	2.8	2.9	5.8	8.2	19	27	30	65	15
n-Hexanol, sat'd with HAcac	1.1	1.2	1.6	1.6	4.1	5.3	10	38	6.0
Aniline-Benzene, 0.1 0.9 m f	3.5	5.5	7.2	9.8	20	32	44	130	24
Chloroform		39		88*		215	257*		210
Benzene anhydrous plus 4 drops of HAcac	6.6	7.2	14	17	50	58	85	155	56

* Probably not saturated

with water since they would be used in a countercurrent extraction system with water The solubility increases with atomic number The data seem to indicate that the separation factors would be greater using chloroform and that this solvent might be the best for countercurrent extraction However, precipitation occurred whenever a few drops of either water or acetylacetone were added to a saturated solution of the chelate in chloroform or benzene The precipitate was identified by chemical analyses and X-ray powder patterns as the monohydrated form of the chelate Hence,

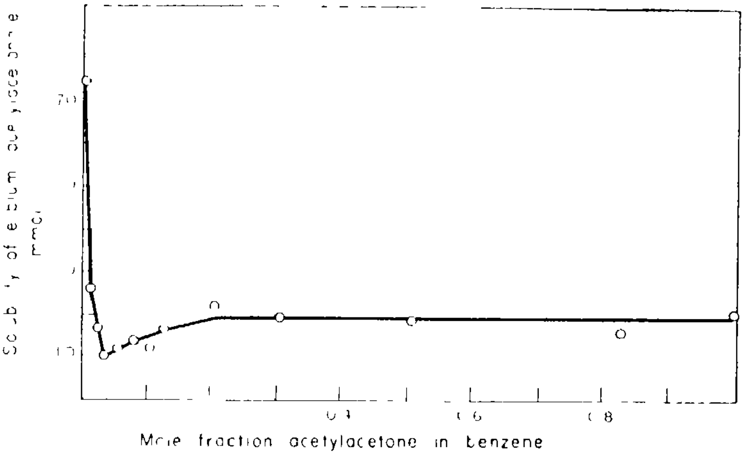


Fig 1 --Solubility of erbium acetylacetonate in benzene-acetylacetone at 30 C

the species in solution cannot be the monohydrated form A logical explanation might be that the hydrated chelate, upon dissolving in the organic solvent, hydrolyzes to give the monobasic chelate

$$Ln(C_5H_7O_2)_3 \cdot H_2O \rightleftharpoons LnOH(C_5H_7O_2)_2 + C_5H_8O_2$$

To test this hypothesis, a benzene solution of erbium acetylacetonate was extracted six times with water, and a positive test for acetylacetone in the extract was obtained when an iron(III) solution was added to give the characteristic deep red color of the iron(III) chelate When the remaining benzene solution was evaporated without heating, the residue was found by chemical analysis and X-ray powder patterns to be the monobasic acetylacetonate Addition of acetylacetone to this residue converted it to the monohydrated compound

When solutions of both the monohydrated and trihydrated chelates of the rare-earths were distilled, an azeotropic mixture of acetylacetone and benzene was obtained in the distillate The remaining solution in the flask yielded the monobasic chelate, the addition of acetylacetone to a portion of the solution in the still pot precipitated the monohydrated chelate When benzene solutions of anhydrous aluminum, or iron(III) acetylacetonates were distilled, no acetylacetone was obtained in the distillate

Apparently then, the rare-earth acetylacetonates undergo hydrolysis readily in most solvents and the hydrolysed form is more soluble than the hydrated chelates If excess chelating agent is added to the solution to repress hydrolysis the solubility decreases markedly Figure 1 shows the solubility of erbium acetylacetonate in benzene-acetylacetone solvent systems A minimum in solubility occurs when the mole ratio of acetylacetone to chelate is approximately 3 to 1 This appears to be

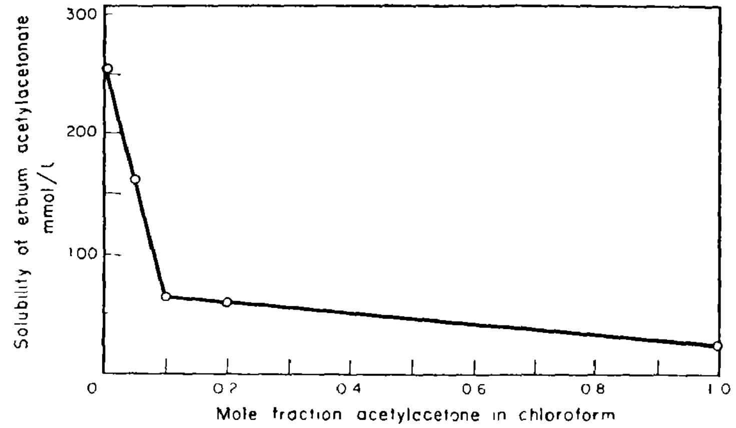


FIG 2 -Solubility of erbium acetylacetonate in chloroform-acetylacetone at 30 C

the concentration of acetylacetone required to suppress the hydrolysis of the chelate to the monobasic form (which is much more soluble in benzene) Figure 2 shows the solubility of erbium acetylacetonate in chloroform-acetylacetone solvent systems Again a rapid decrease in solubility was observed with the addition of acetylacetone up to 0 1 mole fraction Thus the high solubilities in benzene and chloroform are "pseudo" solubilities since they represent the solubility of the hydrolysed form rather than the solubility of the hydrated chelate

Molecular weight determinations of the basic chelates gave high results ranging from 760 to 2950, indicating that polymerization had occurred Table 4 summarizes

TABLE 4 —MOLECULAR WEIGHT STUDY OF SAMARIUM CHELATES

Sample	Solvent	Treatment	Weight of chelate (g)	Weight of solvent (g)	Apparent mol wt
Monohydrate	C_6H_6	Not heated	0 1045	19 33	311
Monohydrate	C_6H_6	Boiled 3 min	0 0946	19 63	474
Trihydrate	C_6H_6	Not heated	0 0913	18 74	198
Trihydrate	C_6H_6	Boiled 3 min	0 1036	16 18	576

Theoretical molecular weight of $Sm(C_5H_7O_2)_3\ H_2O$ 466

The data obtained for molecular weights of the monohydrated and trihydrated forms of samarium acetylacetonates dissolved in benzene with and without boiling the solutions When each of the hydrates is dissolved without heating, low apparent molecular weights are obtained The monohydrate hydrolyzes upon dissolving to release acetylacetone to give the lower freezing point and the trihydrate releases both water of hydration and acetylacetone from the hydrolysis to give an even lower apparent molecular weight When solutions of the chelate are boiled, the released acetylacetone and water are distilled from the solution and the basic chelates are further polymerized to yield high apparent molecular weights The trihydrate polymerizes more rapidly than the monohydrate in boiling benzene

When hydrolysis occurs, countercurrent extractions usually are not reproducible, hence it is necessary to have present in the organic phase an excess of the reagent sufficient to prevent hydrolysis However, this reduces the solubility of the chelate in the organic phase as shown in Figs 1 and 2

Prior to carrying out countercurrent runs, the distribution coefficients of the rare-earth acetylacetonates between acetylacetone as the organic phase and water were determined at a pH of 5.5 and at maximum extraction.⁽⁷⁾ These values are shown in Table 5. There are surprisingly large differences in both the distribution coefficients and the solubilities of the chelates which may be caused by the differences in the solubilities of the hydrates. The hydrates of the lower atomic number rare-earths may be more stable because the larger central ions may be better able to accomodate the water molecules.

TABLE 5. DISTRIBUTION COEFFICIENTS OF THE RARE-EARTH ACETYLACETONATES BETWEEN ACETYLACETONE AND WATER

Chelate	D_{max}	$D_{5.5}$
Yb	7.0	4.6
Er	2.2	1.9
Ho	1.6	1.1
Y	1.2	0.90
Dy	1.15	0.89
Tb	0.94	0.87
Gd	0.64	0.61
Sm	0.47	0.47
Nd	0.41	0.41

The position of the bands in a countercurrent extraction run in a Craig apparatus may be calculated from the equation

$$T_{n,r} = \frac{n!}{r!(n-r)!}\left(\frac{1}{D+1}\right)^{n} D^{r}$$

in which $T_{n,r}$ is the fraction of the metal in tube r after n transfers, and D is the distribution coefficient.

Figure 3 shows the theoretical curves for values of D equal to 0.5, 1.0, 2.0 and 4.5. Figure 4 shows the results of a countercurrent extraction using holmium, erbium, and ytterbium acetylacetonates in a water-acetylacetone system buffered at a pH of 5.5. The organic phase was equilibrated with the aqueous phase containing the acetic acid–sodium acetate buffer adjusted to a pH of 5.5. The three chelates were added in excess to 20 ml of the organic phase, heated to promote solution and allowed to cool. The solution was filtered and 10 ml of the filtrate was used as the organic phase in tube *O*. After the transfers were completed, 5 ml of the organic phase of each tube was evaporated to dryness, and treated with concentrated nitric acid and 30 per cent hydrogen peroxide to remove the organic matter. The residue was dissolved in dilute hydrochloric acid, boiled to remove excess oxidizing agent, buffered to a pH of 9.5, and titrated with a standard solution of EDTA using a standard zinc solution for back-titration with PAN as the indicator. The total rare-earth metal contents in each tube was thus determined. Spectrographic analysis of the residue from each tube determined the distribution of each element in the tubes.

A second countercurrent extraction of the holmium, erbium, and ytterbium acetylacetonates in the same system at a pH of 5.5 is shown in Fig. 5. This run was analysed spectrophotometrically.

⁽⁷⁾ W. B. BROWN, J. F. STEINBACH and W. F. WAGNER, *J. Inorg. Nucl. Chem.* **13**, 119 (1960).

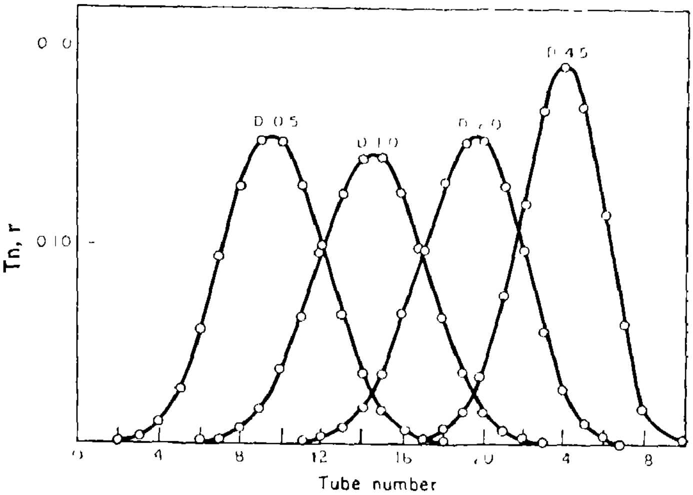


FIG 3 —Theoretical distribution of four chelates with different distribution coefficients

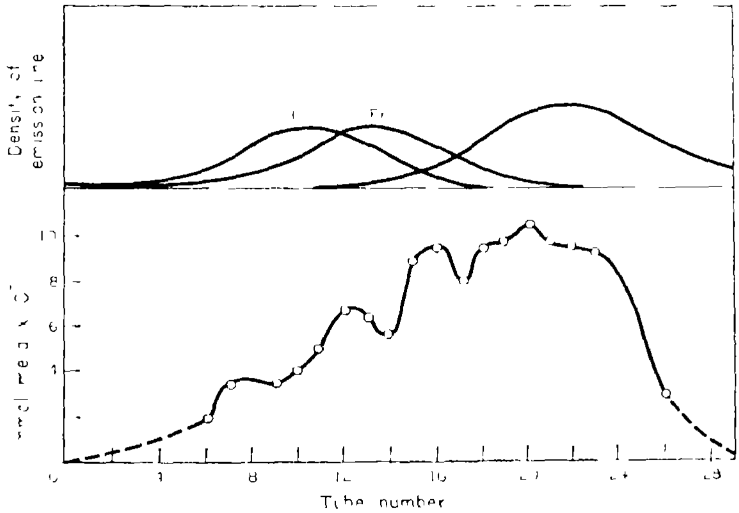


FIG 4 —Countercurrent separation of holmium, erbium and ytterbium acetylacetonates in Water-acetylacetone system buffered at pH of 5 5

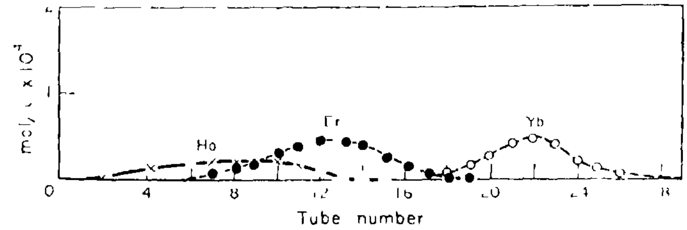


FIG 5 - Countercurrent separation of holmium, erbium and ytterbium acetylacetonates in Water-acetylacetone system at pH of 5 5 Analysed spectrophotometrically

Figure 6 shows the curves obtained for the separation of dysprosium, yttrium and terbium at a pH of 5.5. Analyses were made by use of EDTA titrations and the emission spectrograph.

Figure 7 shows the separation of gadolinium, samarium and neodymium at a pH of 5.5. Neodymium and samarium are so slightly soluble that the amounts extracted were too small to be titrated and were detectable only by the emission spectrograph.

Ytterbium should have its maximum concentration in tubes 23 to 24, experimentally it appears in tube 22. The maxima for erbium and holmium should appear in tubes 19 and 14 respectively; however, these both appeared in lower tubes and gave more diffuse curves than the sharper ytterbium curve. This variance may be due to the effect of the buffer or mixed solute. However, the separability of the rare-earth acetylacetonates is in fair agreement with the behaviour predicted by the foregoing equation. It is easy to separate the highest and lowest members of the rare earths by countercurrent extraction. Neodymium and ytterbium can be separated completely in less than eight transfers. However, complete separation of the adjacent members in the centre of the series such as yttrium, dysprosium and terbium can be accomplished only after more than thirty transfers.

Because of the low solubility of the acetylacetonates in water and the decreased solubility in the organic solvents containing acetylacetone, countercurrent extractions are limited in application. However, the addition of a few mole percent of methanol increases markedly the solubility of the acetylacetonates in both the aqueous and organic phases. Figure 8 shows that the solubility of erbium acetylacetonate in water increases as methanol is added. The heavier rare-earth chelates are very soluble in methyl alcohol. Relatively large amounts of the chelates can be dissolved in chloroform, making this solvent desirable for large scale separations. By utilizing the solubility relationships discovered in this study it was possible to develop a chloroform-water system having the advantages of high solubility of the chelates and control over the partition coefficients. It is possible to repress the solvent power of the chloroform by adding acetylacetone which also suppresses hydrolysis. The solvent power of the aqueous phase can be increased by the addition of methanol which leads to the formation of the more soluble methanol-solvated chelate. Accordingly, a two phase system composed of the four components, acetylacetone, chloroform, methanol and water was devised having the advantage of high solubility for the chelates and adjustment of the distribution between the phases to a value of about unity. Table 6 lists the three systems used for the countercurrent extraction studies at different acidities. The methanol distributes almost entirely in the aqueous phase whereas the acetylacetone is found predominantly in the chloroform phase.

TABLE 6. COMPOSITION OF QUATERNARY COMPONENT SOLVENT SYSTEM FOR COUNTERCURRENT EXTRACTIONS

	Composition (mole per cent)		
Component	Unbuffered system	Buffered at pH 4.9	Buffered at pH 5.5
Water	75.0	67.2	67.1
Chloroform	17.0	18.3	18.2
Acetylacetone	2.7	2.4	2.5
Methanol	5.6	12.1	12.2

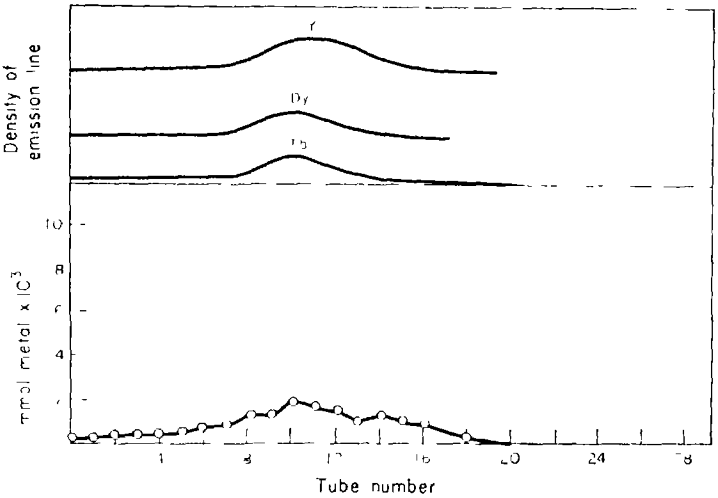


Fig. 6 Countercurrent separation of dysprosium, yttrium and terbium acetylacetonates in water acetylacetone system buffered at pH of 5.5

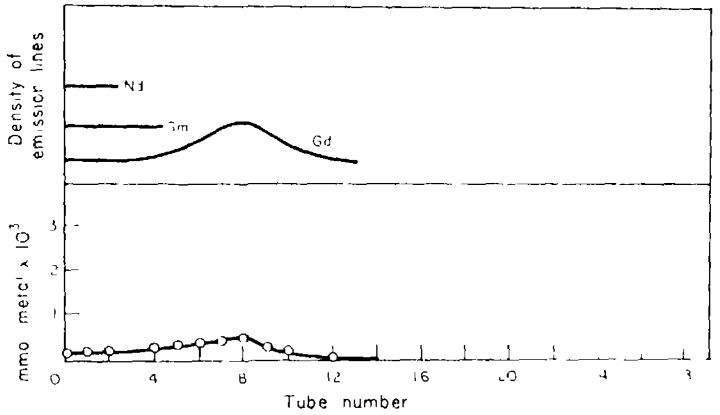


Fig. 7 Countercurrent separation of gadolinium, samarium and neodymium acetylacetonates in water acetylacetone system buffered at pH of 5.5

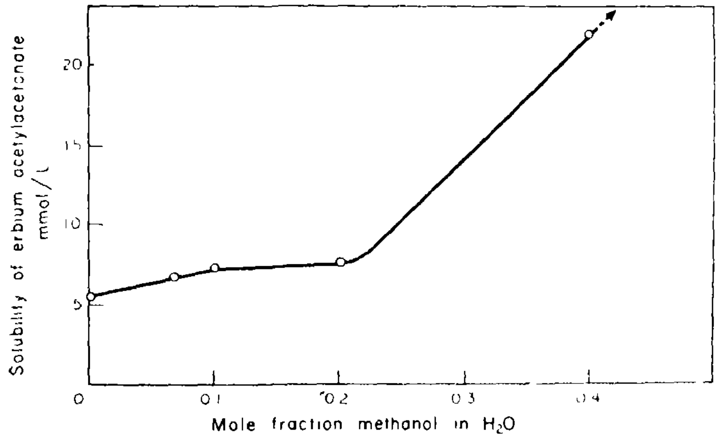


Fig. 8 —Solubility of erbium acetylacetonate in water–methanol at 30 °C

The countercurrent extraction of erbium, holmium, and dysprosium acetylacetonates using the unbuffered system is shown in Fig 9 Ten ml of each phase were saturated with the three chelates and added to tube O of the apparatus After thirty transfers the contents of each tube were analysed by the spectrophotometric and spectrographic techniques

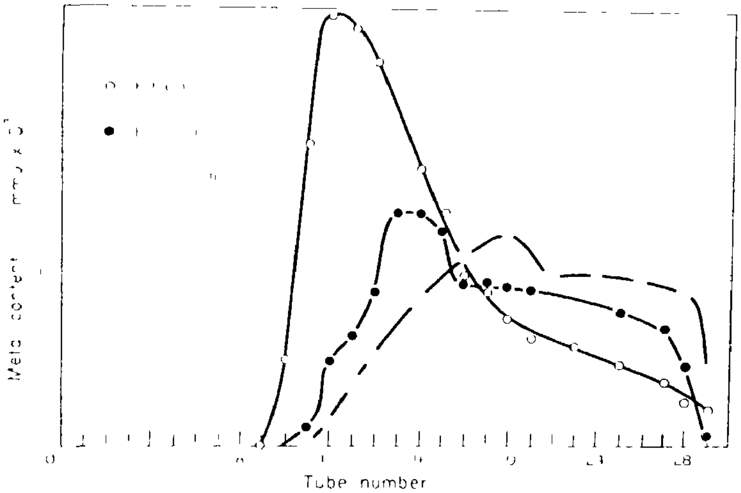


FIG 9 Countercurrent separation of erbium, holmium, and dysprosium acetyl acetonates in an unbuffered four-component system

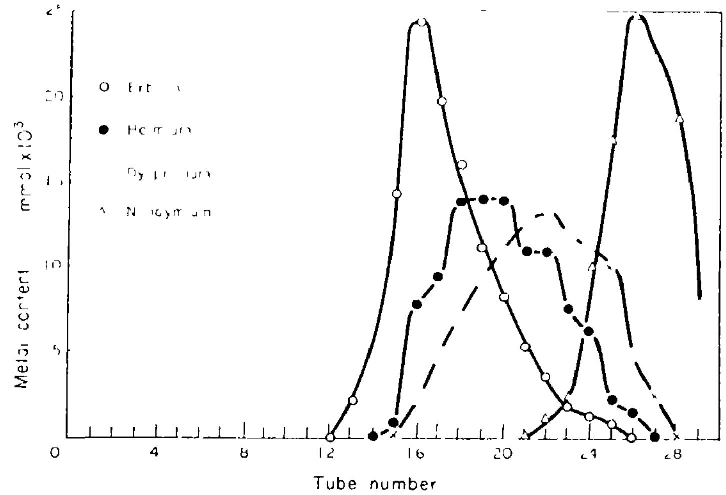


FIG 10 - Countercurrent separation of erbium, holmium dysprosium and neodymium acetylacetonates in a four-component system buffered at pH of 4 9

Figure 10 shows the countercurrent extraction curves for the erbium, holmium, dysprosium and neodymium chelates in the system buffered at a pH of 4 9 using a sodium acetate-acetic acid buffer

Figure 11 shows the extraction of the erbium, holmium, dysprosium, and neodymium chelates at a pH of 5 5

A comparison of Figs 9, 10 and 11 shows that buffering sharpens the separations There seems to be a slight improvement in separation at a pH of 5 5 compared to a pH of 4 9 While the separation was not greatly enhanced over that obtained in

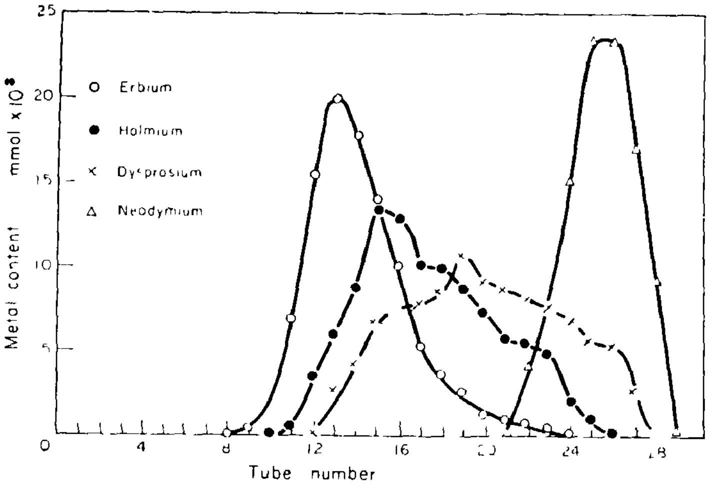


FIG. 11 —Countercurrent separation of erbium, holmium, dysprosium and neodymium acetylacetonates in a four-component system buffered at pH of 5 5

the acetylacetone–water system, over ten times the total quantity of chelates can be dissolved in the system by increasing the concentration of the methanol

In summary, it may be said that the acetylacetonates of the rare-earths are amenable to countercurrent extraction procedure Both hydrolysis and solvation of the chelates play an important role in the process and probably warrant further study

Acknowledgement—The authors express their gratitude to the Atomic Energy Commission for support of this work on Contract No AT(40-1)2124

J Inorg Nucl Chem 1963 Vol 25, pp 441 to 446 Pergamon Press Ltd Printed in Northern Ireland

THE EXTRACTION OF URANIUM(VI) FROM SULPHURIC ACID SOLUTIONS BY TRI-N-OCTYLAMINE

TAICHI SATO
Government Chemical Industrial Research Institute, Honmachi, Shibuya-ku,
Tokyo, Japan

(*Received* 10 *May* 1962, *in revised form* 30 *August* 1962)

Abstract—The partition of uranium(VI) between sulphuric acid solutions and solutions of tri-n-octylamine (TOA) in benzene has been investigated at varying concentrations of sulphuric acid, solvent and uranium and at different temperatures The extraction of sulphuric acid and the water content of the organic phase have also been examined, and infra-red spectral studies made of the organic solutions The mechanism of uranium extraction is discussed on the basis of the results obtained

THE mechanism of uranium(VI) extraction from sulphuric acid solutions by tri-n-dodecylamine (TDA) has been discussed in a previous paper,[1] the present study has been made to obtain information on the extraction by tri-n-octylamine (TOA)

EXPERIMENTAL

TOA (the Kao Soap Co , Ltd) was diluted with benzene The procedures for obtaining partition coefficients, the determination of acidity in the organic phase and the infra-red spectral measurement were the same as those described previously [1] The water content of the organic phase was determined by a Karl Fischer titration

RESULTS AND DISCUSSION

The same variables were investigated as in the case of TDA,[1] as the results obtained are similar to those for TDA, it is presumed that the mechanism of uranium extraction by TOA is the same as that for TDA

Dependence on solvent and uranium concentrations

The extraction of uranyl sulphate solution (5 g/l) containing sulphuric acid at various concentrations with solutions of TOA in benzene at 20°C gave the results shown in Fig 1 These resemble the results obtained with TDA,[1] but the maximum in the partition coefficient appears at about 0 1 M initial acidity As uranium(VI) is extracted less efficiently by TOA, it is assumed that the efficiency of extraction by tertiary alkyl amines increases with the length of the attached alkyl chain

The variation in the organic phase uranium concentration with the initial aqueous uranium concentration in 0 1 M sulphuric acid (where the partition coefficient is a maximum) was examined with 0 1 M TOA in benzene, with the results shown in Fig 2 Similar isotherms were obtained for extraction from 0 05 and 0 3 M sulphuric acid solutions These results suggest that four amine molecules are associated with each uranium ion This is supported by the dependence of the partition coefficient on the solvent concentration derived from Fig 1 the slopes of plots of log E_a^0 vs log (C_N 4C_U), in which E_a^0 is the partition coefficient, C_N the total amine concentration and C_U the organic uranium concentration, in 0 5, 1 0 and 2 0 M sulphuric acid are 1 4, 1 3 and 1 0 respectively In addition, the values of C_U vs C_N in 0 01 and 0 02 M sulphuric acid are similar to those for TDA (1)

---

[1] SATO, *J Inorg Nucl Chem* In press

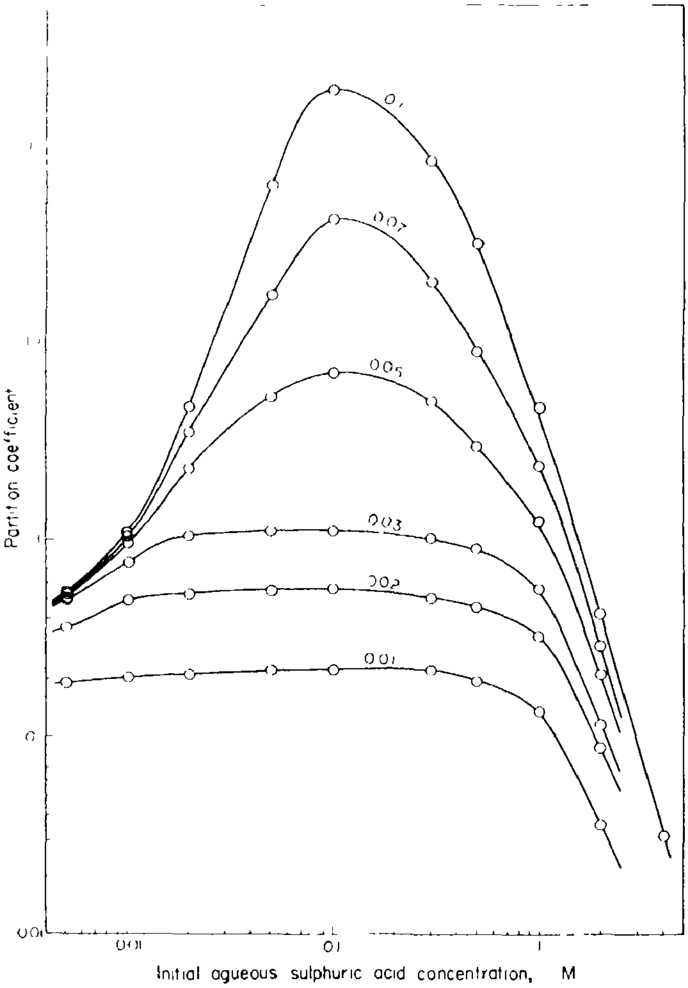


FIG 1 —Effect of solvent concentration upon the extraction of uranium(VI) from sulphuric acid solutions of various concentrations by TOA in benzene (figures on curves are TOA concentrations, M)

Extraction of sulphuric acid and water content of organic phase

The acidity and water content of the organic phase was measured after the extraction of uranyl sulphate solution (5 g/l) containing sulphuric acid at various concentrations with 0 1 M TOA in benzene at 20°C Similar experiments were made for the extraction of sulphuric acid solutions in the absence of uranium The results are given in Figs 3 and 4 In the extraction of sulphuric acid from 0 5 and 2 0 M solutions with solutions of TOA in benzene, the slopes of log (H_2SO_4 distribution ratio) vs log (initial TOA concentration) were nearly unity, as in the case of TDA[1]

In the absence of uranium, by analogy with TDA, it is expected that the extraction may be represented by the equations $H_2SO_4(a) + 2R_3N(o) \rightleftharpoons (R_3NH)_2SO_4(o)$ at low

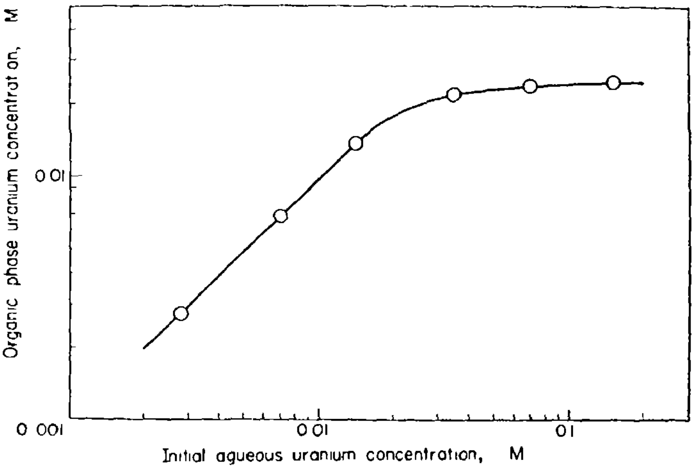


FIG 2 —Variation of organic phase uranium concentration with the initial aqueous uranium concentration for the extraction of uranium(VI) from 0.1 M sulphuric acid solution by 0.1 M TOA in benzene

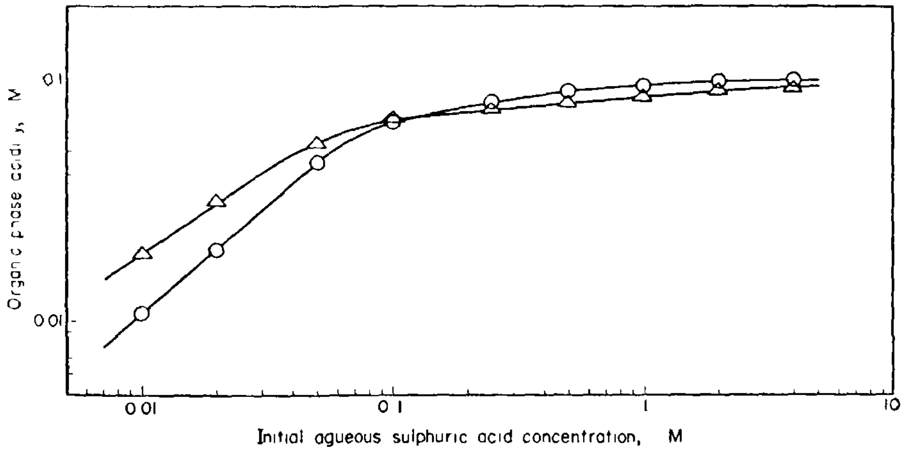


FIG 3 —Change in acidity of organic phase caused by the extraction of uranium(VI) with 0.1 M TOA in benzene (○ in the absence of uranium, △ in the presence of uranium)

acidities and $(R_3NH)_2SO_4(o) + H_2SO_4(a) \rightleftharpoons 2(R_3NH)HSO_4$ at high acidities, (a) and (o) denote aqueous and organic phases respectively, and R represents C_8H_{17} In the presence of uranium, below 0.1 M initial acid the acidity of the organic phase is higher than that in the absence of uranium, but the situation is reversed above 0.1 M This implies that the mechanism of extraction at low acidities is different from that at high acidities From Fig. 4 it is inferred that the hydrated amine sulphate is gradually replaced by the unhydrated amine bisulphate as the acidity is further increased, and that the water content of the organic phase is diminished by the formation of the amine-uranyl sulphate complex

Temperature effect

The extraction of uranyl sulphate solution (5 g/l) containing 0 02 and 1 0 M sulphuric acid with 0 1 M TOA in benzene at temperatures between 10 and 50°C gave the results shown in Fig 5

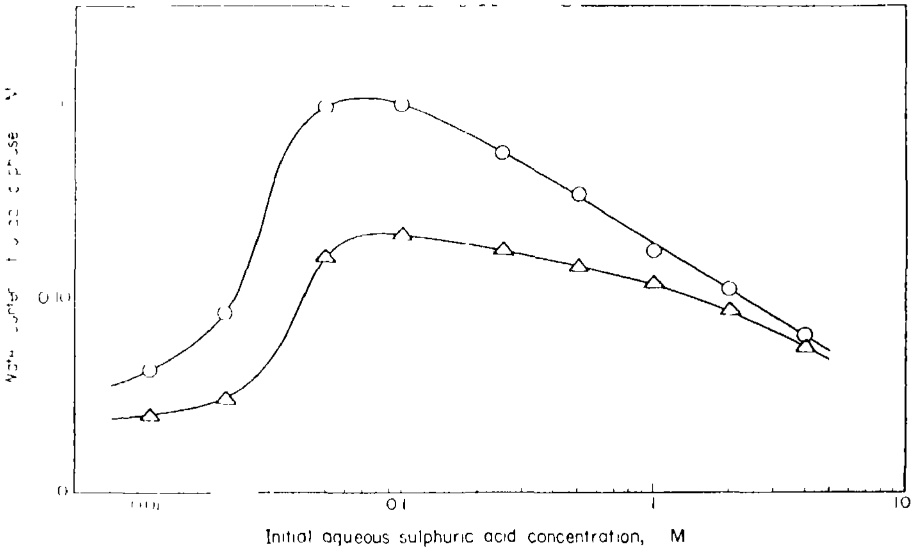


FIG 4 —Change in water content of organic phase caused by the extraction of uranium-(VI) with 0 1 M TOA in benzene (○ in the absence of uranium, △ in the presence of uranium)

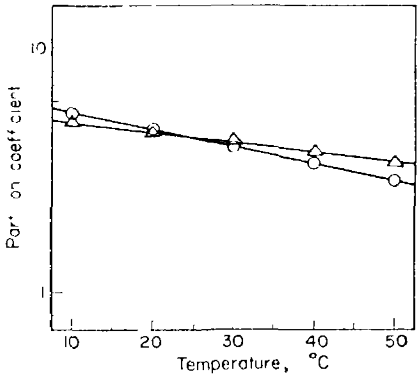


FIG 5 —Effect of temperature upon the extraction of uranium(VI) from sulphuric acid solution by 0 1 M TOA in benzene (△ and ○ denote the sulphuric acid concentrations of 0 02 and 1 0 M respectively)

Infra-red spectra

The organic phases from the extraction with 0 1 M TOA in benzene of uranyl sulphate solutions (5 and 25 g/l) containing sulphuric acid at various concentrations were examined by infra-red spectroscopy, similar measurements were made in the absence of uranium The spectra for extractions in the presence of uranium are shown in Fig 6 The spectra obtained in both cases closely resemble those for TDA,[1] with increasing acidity, in the absence of uranium, the sulphate ion frequencies[2] at 1140, 1090, 1025 and 960 cm^{-1} become weaker, and the bisulphate ion frequencies[2] at 1240, 1150, 1055 and 850 cm^{-1} show a progressive increase in intensity

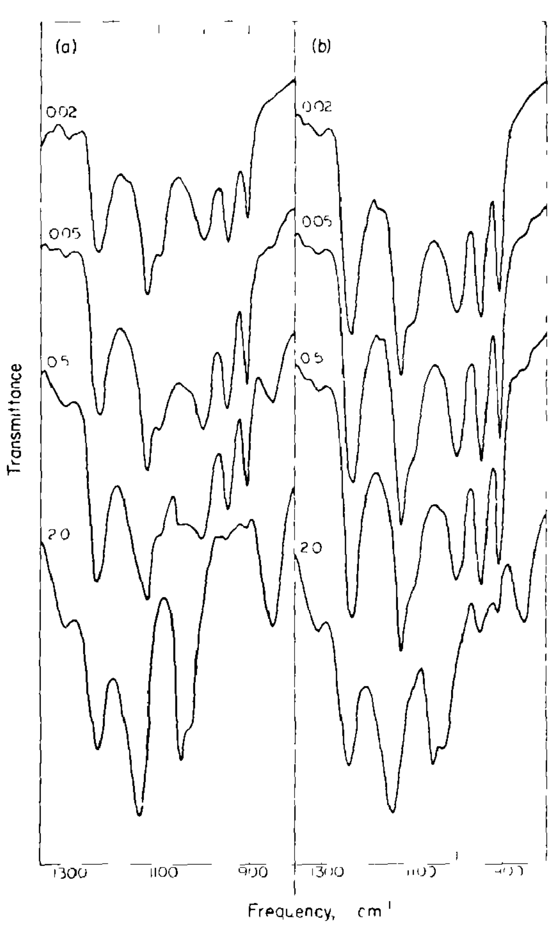


Fig 6 – Infra-red spectra of the organic solutions involved in the extractions of uranyl sulphate solutions containing sulphuric acid of various concentrations with 0 1 M TOA in benzene (figures on curves are sulphuric acid concentrations, M)
(a) 5 g/l uranyl sulphate solution
(b) 25 g/l uranyl sulphate solution

In the presence of uranium (Fig 6) the band at 945 cm^{-1} is assigned to the asymmetric stretching frequency of the uranyl group,[3] and the bands at 1235 1120, 1095, 1000 and 905 cm^{-1} to the vibrational frequencies of the sulphato group, indicating a lower symmetry than that in the sulphate ion due to covalent bonding to the uranyl ion

---

A Miller and C H Wilkins, *Analyt Chem* **24**, 1253 (1952) G E Walrafen and D M Dodd, *Trans Faraday Soc* **57**, 1286 (1961)

g, B M Gatehouse and A E Comyns, *J Chem Soc* 3965 (1958), G L Caldow, A B VanCleave and R L Eager, *Canad J Chem* **38**, 772 (1960)

Stoichiometry of the amine uranyl sulphate complex and the mechanism of uranium extraction

Chemical analysis of the solvent phase from the extraction of UO_2SO_4 (50 g/l.) containing 0.05 M H_2SO_4 with 0.1 M TOA in benzene, which the data indicated to be practically pure complex, showed the composition of the latter to be 1U : 3SO_4 : 4 amine : 3H_2O. The stoichiometry of the amine uranyl sulphate complex was thus indicated to be $(R_3NH)_4UO_2(SO_4)_3(OH_2)_3$, i.e., $[(R_3NH)_2SO_4]_2 \cdot UO_2SO_4(OH_2)_3$.

The following mechanism is suggested for the extraction of uranium(VI) from sulphuric acid solutions by TOA: *at low acidities* $UO_2SO_4(a) + 2(R_3NH)_2SO_4(o) \rightleftharpoons (R_3NH)_4UO_2(SO_4)_3(o)$, and *at high acidities* $UO_2SO_4(a) + 4(R_3NH)HSO_4(o) \rightleftharpoons (R_3NH)_4UO_2(SO_4)_3(o) + 2H_2SO_4(a)$. From the data shown in Fig. 5, the heat of reaction (change in enthalpy) was calculated to be 2.06 kcal/mole in 0.02 M H_2SO_4 and 8.25 kcal/mole in 1.0 M H_2SO_4. These values are analogous to those for TDA.(1)

Acknowledgements—The author wishes to thank Mr. H. WATANABE and Mr. M. NISHIZAKI, who carried out much of the experimental work. He also thanks the Kao Soap Co., Ltd. for a gift of tri-n-octylamine.

J. Inorg. Nucl. Chem. 1963, Vol. 25, pp. 447 to 452. Pergamon Press Ltd. Printed in Northern Ireland

ION-EXCHANGE BEHAVIOUR OF THE TRANSURANIUM ELEMENTS IN $LiNO_3$ SOLUTIONS*

S. ADAR,† R. K. SJOBLOM, R. F. BARNES and P. R. FIELDS
Argonne National Laboratory, Argonne, Illinois

and

E. K. HULET and H. D. WILSON
Lawrence Radiation Laboratory, Livermore, California

(*Received* 2 *July* 1962, *in revised form* 6 *September* 1962)

Abstract—The distribution coefficients (K_D's) of the trivalent actinide elements Pu, Am, Cm, and Cf between $LiNO_3$ solutions (containing 0.005 M H^+) and Dowex-1 anion resin were measured. A column separation of Am and Cm using this system was investigated at 22.5°C and 87°C and the separation factor was found to be substantially higher than that obtained with the complexing agent ammonium α-hydroxyisobutyrate and cation exchange resin.

THE separation of the transplutonium elements is becoming an increasingly important problem as the production of these elements is expanded. For example, long lived isotopes of americium and curium in almost gramme quantities were produced by irradiating a plutonium fuel assembly in the Materials Testing Reactor for two years. Processing of the assembly yielded approximately 600 mg of ^{244}Cm and 1.3 g of ^{243}Am. A more recent programme has produced several hundred grammes of ^{243}Am and ^{244}Cm but these materials have yet to be separated from the plutonium fuel and the accompanying fission products. Re-irradiation of some of these elements will eventually yield hundreds of milligrams of berkelium and californium. To meet the increasing demand for a better actinide element separation, a new ion exchange system was investigated and the results are reported in this article.

Earlier work by MARCUS(1, 2) has shown that the rare earth elements can be separated from each other using Dowex-1 anion resin as an adsorbent and $LiNO_3$ solutions as an eluant. A similar technique applied to the separation of the actinide elements is described in this paper. Typical actinide elements such as plutonium, americium, curium and californium were studied. Particular emphasis was placed on the transplutonium elements americium and curium which are being produced in large quantities and are difficult to separate from each other.

Equilibrium experiments were performed at room temperature to measure the distribution coefficients of the actinide elements between Dowex-1 resin and $LiNO_3$ solutions of varying concentrations. The resin used in these experiments was Bio-Rad (Dowex) AG 1-X8, 200–400 mesh. The resin was graded rather crudely by batch settling in distilled water to remove the very fine resin particles. The resin was then washed in a column with 2 M NH_4OH, then washed successively with water, 1 M HNO_3, 15 M HNO_3, and again with water. Finally the resin was dried in an oven at 110°C to constant weight. The equilibrium experiments were usually agitated, at room temperature for a minimum of two hours. Tracer tests with Pu(IV) showed that equilibrium was reached within 2 hours.

---

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

† Present address, Israel Atomic Energy Commission, Tel Aviv, Israel.

(1) Y. MARCUS and F. NELSON, *J. Phys. Chem.* **63**, 77 (1959).

(2) Y. MARCUS and I. ABRAHAMER, *J. Inorg. Nucl. Chem.* **22**, 141 (1961).

Reproducible distribution coefficients,

$$K_D = \frac{\text{Concentration of solute/g of resin}}{\text{Concentration of solute/ml of solution}}$$

were obtainable only when considerable care was taken with the assaying of the very viscous salt solutions and when the amount of salt on the final assay plate was insufficient to cause substantial absorption of the α-particles (less than 0.1 mg). Attempts to precipitate the actinide elements as hydroxides from the LiNO$_3$ solutions using ferric ion as the carrier, followed by removal of the Fe(III) ions by solvent extraction, usually led to higher K_D's. Other techniques, such as direct solvent extraction of the actinide elements from the LiNO$_3$ solutions, also had complications and gave higher K_D's.

The tracers used for these investigations were carefully purified by ion exchange techniques and analysed radiochemically for other radioactive species.

Stock solutions of Pu(IV) were prepared by standard techniques such as treatment with H_2O_2 or potentiometric reduction of Pu(VI). The absorption spectrum of the stock solution to be used was analysed with a Cary Model 14 Spectrophotometer before tracer solutions of Pu(IV) were prepared.

Pu(III) was prepared by reducing Pu(IV) solutions with ferrous sulphamate. An excess of ferrous sulphamate as a holding reductant was necessary to prevent the slow oxidation of Pu(III) to Pu(IV). To insure that only Pu(III) was represented in the measurements, the initial and final LiNO$_3$ solutions from the equilibration experiments were extracted with thenoyltrifluoroacetone which, under the proper conditions, extracts only Pu(IV). Since Pu(III) will also extract from LiNO$_3$ (0.005 M H^+) solution, the hydrogen ion concentration was adjusted to about 0.5 M before extraction.

The distribution coefficients of the trivalent actinide elements plutonium, americium, curium and californium are shown as a function of lithium nitrate (containing 0.005 M H^+) concentration in Fig. 1. The adsorption of Pu(IV) by the resin was approximately ten times that of Pu(III) at 1 M LiNO$_3$, the only concentration where the two valence states were compared. It was found that the distribution coefficients decrease rapidly as the [H^+] concentration of the LiNO$_3$ solutions increases above 0.01 M. A more detailed study of this effect with rare earth elements has been reported by MARCUS.(1,2) From Fig. 1 it can readily be seen that the distribution coefficients increase with increasing LiNO$_3$ concentration, and at constant molarity the distribution coefficients decrease with increasing atomic number, a reversal of the order observed in LiCl solutions.(3)

Comparing the K_D's reported here with the results of MARCUS(1,2), it is apparent that the LiNO$_3$–Dowex-1 system will not be as effective as LiCl–Dowex-1(3) in separating the actinide elements from the rare earths due to the overlap in K_D's of many of the elements in both series. However, it should be noted that the ratio

---

(3) E. K. HULET, R. G. GUTMACHER and M. S. COOPS, *J. Inorg. Nucl. Chem.* **17**, 350 (1961).

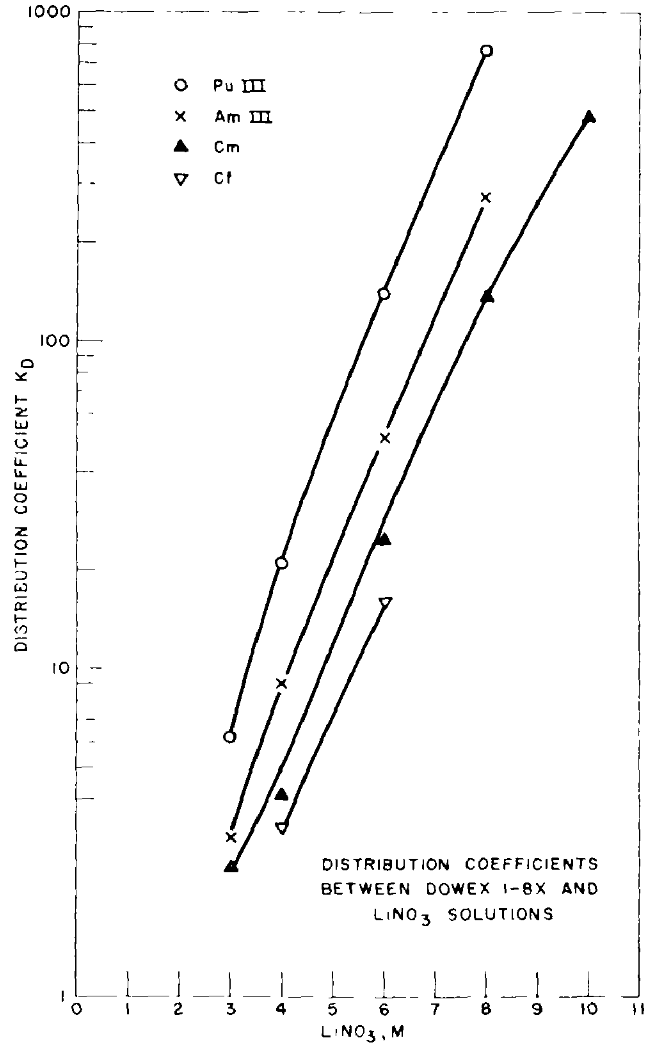


FIG 1 - Distribution coefficients of trivalent actinides between $LiNO_3$ (0 005 M H^+) solutions and Dowex 1-X8 resin

$\{K_D[Am(III)]\}/\{K_D[Cm(III)]\} \simeq 2$ found in this work would predict a better separation of these two elements than in the ammonium α-hydroxy isobutyrate–Dowex 50[4–6] system used so widely in separating trivalent actinides

Column elutions were made with tracer solutions to investigate the separation of Am and Cm under dynamic conditions In order to elute these elements in a reasonable time the range of 4-5 M $LiNO_3$ as the eluant was chosen Hydraulically graded Dowex-1 resin with an 0 8 to 1 5 cm/min settling rate was selected as the adsorbent The actinide elements were strongly adsorbed on the resin bed from 8 M $LiNO_3$ (0 01 M $[H^+]$), and then eluted with the more dilute 4 2 M $LiNO_3$ (pH 2 1) The

---

G R CHOPPIN, B G HARVEY and S G THOMPSON, *J Inorg Nucl Chem* **2**, 66 (1956)

H L SMITH and D C HOFFMAN, *J Inorg Nucl Chem* **3**, 243 (1956)

J MILSTED and A B BEADLE, *J Inorg Nucl Chem* **3**, 248 (1956) columns were operated at 87°C, principally to increase the rate of exchange an narrow the elution peaks Fig 2 shows a typical column run Smaller Am and C distribution coefficients were found from numerous column elutions at 87°C tha those obtained in equilibrium studies at room temperature In addition, colum elutions at room temperature (Fig 3) indicated not only greater adsorption by th

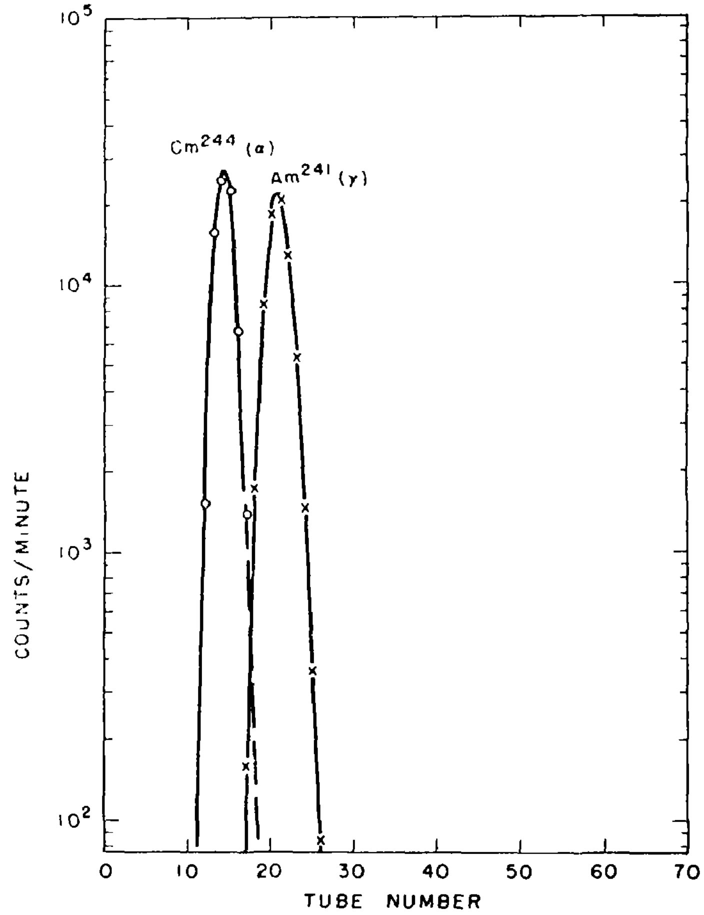


Fig 2 —Column separation of trace amounts of Am and Cm at 87°C 4 2 M $LiNO_3$ - 0 01 M H^+ and Dowex 1-X8 resin Resin settling rate 8–15 mm/min Column size 9 cm 6 mm Flow rate 0 38 ml/cm² sec and tube volume 0 433 ml/tube

resin but also a larger separation factor, $\{K_D[Am(III)]\}/\{K_D[Cm(III)]\}$, (Table than could be obtained at elevated temperatures Further reduction in peak width would be of greater advantage in utilizing the superior separation found in roo temperature elutions

A mixture containing 20 mg of ^{244}Cm and 40 mg of ^{243}Am was selected to tes the usefulness of the $LiNO_3$ with macro amounts of americium and curium Th mixture, containing a large amount of inert salts, resulted from the isolation by io exchange of 600 mg of curium and 1 2 of americium from an irradiated plutoniu fuel assembly A feed solution made by dissolving the material in 6 ml of saturated

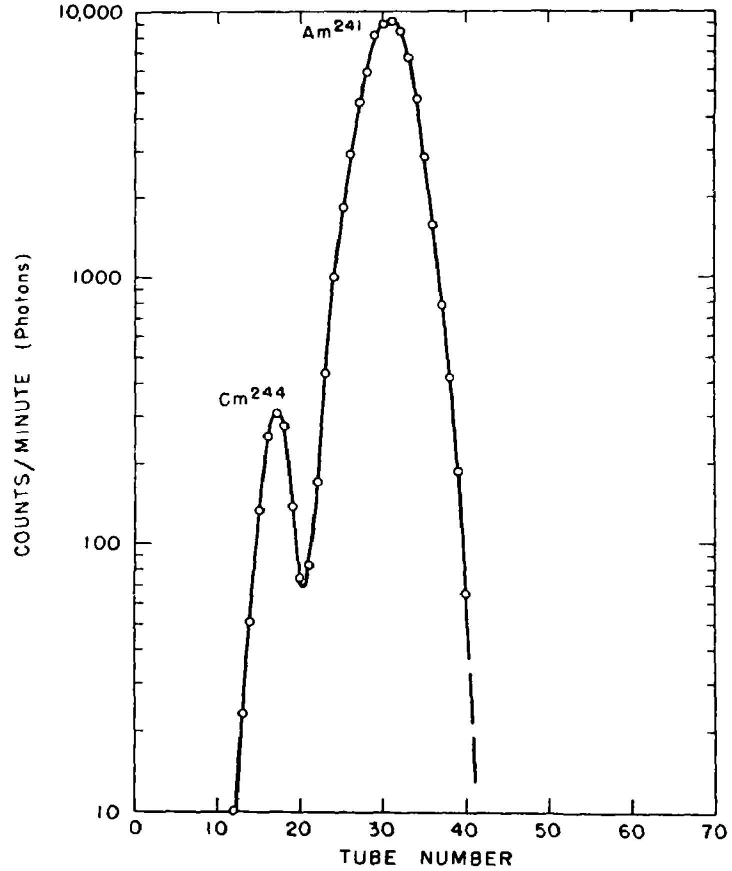


FIG. 3 Column separation of trace amounts of Am and Cm at 22.5°C 4.2 M $LiNO_3$ + 0.01 M H^+ and Dowex 1-X8 resin Resin grade 8–15 mm/min Column size 9 cm × 6 mm Flow rate 0.16 ml/cm² sec and tube volume 0.461 ml/tube

$LiNO_3$ (pH 2.1) was transferred onto a 1 cm diameter by 11 cm long resin bed maintained at 87°C. After adsorption the actinides were eluted with 4.2 M $LiNO_3$ (pH 2.9) with the results shown in Fig. 4. A good separation of americium from curium as well as from the inert impurities was attained. It was observed that the salts remained on the top of the resin bed and were later eluted with 1 M HNO_3, however, no α-activity was found in this fraction. Americium and curium were recovered from the $LiNO_3$ solutions by precipitation as the hydroxides with NH_4OH.

The $LiNO_3$–Dowex-1 system appears promising as a separation technique for the transuranium elements. For high concentrations of americium and curium the

TABLE 1

Temp (°C)	K_D[Am (III)]	K_D[Cm (III)]	$\frac{K_D[\text{Am (III)}]}{K_D[\text{Cm (III)}]}$
22.5	10.2	5.3	1.9
87	6.1	3.9	1.6

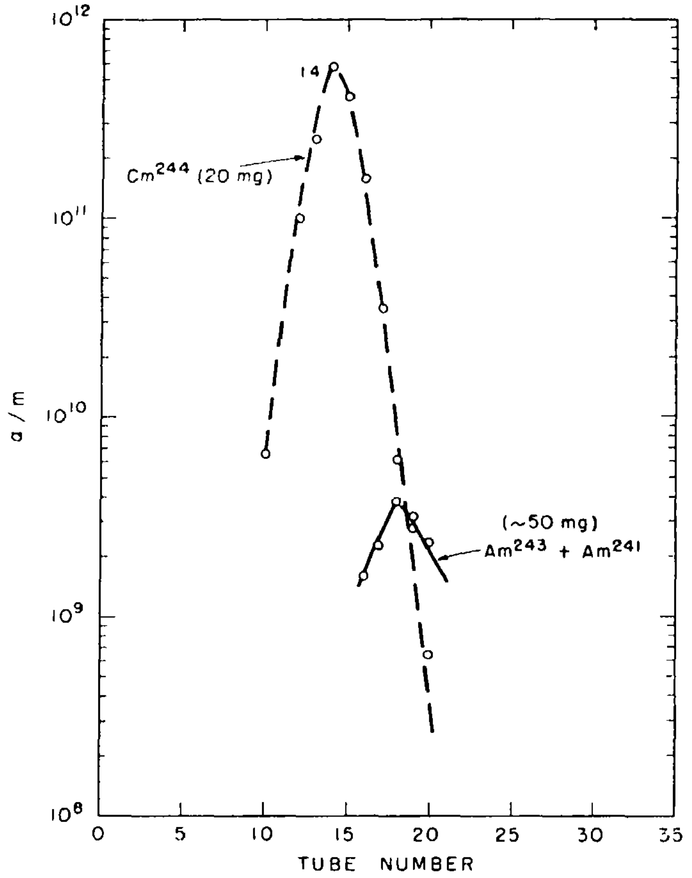


FIG 4 Column separation of milligram amounts of Am and Cm at 87 C 4 2 M $LiNO_3$ 0 01 M H^+ and Dowex 1-X8 resin Resin settling rate of 0 5–0 8 cm/min Column size 1 cm 11 cm Flow rate 4 ml/5 min and tube volume 2 ml/tube

$LiNO_3$-Dowex-1 system gave better separations than either the ammonium α-hydroxy isobutyrate-cation column or the oxidation of americium by persulphate(7) or ozone(8) In the latter cases, the oxidation of americium is difficult in the presence of H_2O_2 generated by the intense alpha activity, whereas the $LiNO_3$ separation is not adversely influenced Generally, ion-exchange column operations, such as the one described, are well suited for remote control use in shielded facilities

(7) L B ASPREY, S E STEPHANOU and R A PENNEMAN, *J Amer Chem Soc* **73**, 5715 (1951)

(8) R A PENNEMAN, J S COLEMAN and T K KEENAN, *J Inorg Nucl Chem* **17**, 138 (1959)

J Inorg Nucl Chem , 1963, Vol 25, pp 453 to 459 Pergamon Press Ltd Printed in Northern Ireland

HYDROLYTIC REACTIONS OF TETRASULPHUR TETRANITRIDE IN A HOMOGENEOUS MEDIUM

C G R Nair and A R V Murthy
Department of Inorganic and Physical Chemistry,
Indian Institute of Science, Bangalore 12, India

(*Received* 20 *July* 1962, *in revised form* 28 *August* 1962)

Abstract—The hydrolytic reactions of tetrasulphur tetranitride are studied in a homogeneous medium Alkaline hydrolysis gives sulphite, thiosulphate, sulphate and sulphide whereas the products in acid hydrolysis are mainly sulphur dioxide, elemental sulphur and hydrogen sulphide, with traces of polythionates Under optimum conditions, tetrasulphur tetranitride reacts with sulphite consuming 2 moles of sulphite per mole of sulphur nitride to give 2 moles of trithionate The reaction of sulphur nitride with thiosulphuric acid gives pentathionate and tetrathionate

THE constitution of tetrasulphur tetranitride has been the subject of much discussion and the hydrolytic reactions of the compound are of special interest since they furnish the main chemical evidence for its constitution The hydrolysis of sulphur nitride has been investigated by GOEHRING(1), who carried out two-phase hydrolytic studies by shaking solid sulphur nitride with benzene and an aqueous solution of the appropriate reagent The reactions under these conditions are slow and require mechanical shaking for several hours Sulphite, thiosulphate and trithionate were found to be the products of alkaline hydrolysis, trithionate was observed only in weakly alkaline solutions Trithionate was found to be the major product of the reaction of sulphur nitride and sulphite, a small quantity of thiosulphate was also observed in this reaction During all these reactions, Goehring observed that the entire quantity of nitrogen was converted into ammonia

The difficulties of the two-phase studies can be obviated and the experimental technique can be simplified by working in a homogeneous medium Such a homogeneous medium can be obtained by using suitable solvents For instance, the two-phase system (benzene–water) adopted by GOEHRING can be easily homogenized by the addition of a sufficient quantity of alcohol The hydrolytic reactions under these conditions have been found to be quite rapid and quantitative Similar experimental results were obtained when sulphur nitride was dissolved in dioxan and shaken with aqueous reagents As dioxan is completely miscible with water the system would be homogeneous, it may be pointed out that dioxan is also a better solvent for sulphur nitride than benzene

The hydrolytic reactions of sulphur nitride in alkaline and acid media as well as in the presence of sodium sulphite and thiosulphate are described in the present communication

EXPERIMENTAL

Tetrasulphur tetranitride was prepared by the reaction of ammonia with disulphur dichloride as described by GOEHRING [2] The product was twice recrystallized from extra-pure benzene The melting point of the pure sample was found to be 177° (reported(2) 178) Analysis for nitrogen and sulphur

---

M GOEHRING, *Ber Dtsch Chem Ges* **80**, 110 (1947)

M BECKE-GOEHRING, *Inorganic Synthesis*, Vol 6, p 124 Interscience New York (1960) showed 69 31 per cent sulphur and 30 26 per cent nitrogen, theoretical 69 61 % S and 30 40 % N

The solvents benzene, dioxan and alcohol were purified by standard methods (3) Other reagents used were all of the analytical reagent grade

General procedure

A known weight of the sulphur nitride was dissolved in 10 ml of benzene and 40 50 ml of an aqueous solution of carbonate-free sodium hydroxide (or hydrochloric acid, sodium sulphite or sodium thiosulphate depending upon the particular reaction under study) were added The immiscible liquid system was then homogenized by the addition of 65 75 ml of alcohol and the contents were shaken well It was found convenient to use dioxan instead of benzene as solvent, in this case the addition of alcohol was not necessary for the sake of homogenization, yet alcohol was added in some experiments so as to serve as an inhibitor of the atmospheric oxidation of sulphite (4) All the experiments were conducted at room temperature (28 2 C)

After the completion of the reaction the products were analysed following the analytical procedures of KURTENACKER and co-workers(5) for a mixture of sulphide sulphite thiosulphate and polythionates and of Geohring, Feldmann and Helbing(6) for a mixture of polythionates The total sulphur in solution was estimated as barium sulphate after oxidation with either sodium peroxide or bromine and nitric acid

Preliminary experiments showed that hydrogen sulphide and sulphur dioxide were among the products in acid hydrolysis To prevent the escape of these gaseous products, the experiments were carried out in an all-glass apparatus fitted with suitable ground-glass joints and leads and the gaseous products were swept off by a stream of pure nitrogen and absorbed in an alkaline suspension of cadmium hydroxide The cadmium hydroxide helped to fix the hydrogen sulphide as cadmium sulphide immediately on absorption, the sulphur dioxide was fixed as alkali sulphite which remained in solution No thiosulphate is produced when the mixed gases are absorbed in alkali containing cadmium hydroxide The sulphide and sulphite were then iodometrically determined (4)

The analytical results of alkaline and acid hydrolyses are presented in Tables 1 and 2 respectively while Tables 3 and 4 give the results of hydrolytic reactions in presence of sodium sulphite and thiosulphuric acid respectively Blank experiments were conducted in each case There was no need for

TABLE 1 - ALKALINE HYDROLYSIS OF TETRASULPHUR TETRANITRIDE
(Over-all alkali strength 0 50 N)

Expt no *	Amount of sulphur nitride taken†	Sulphide† (%)	Sulphite† (%)	Thiosulphate† (%)	Sulphate† (%)	Total sulphur found (%)
1	24 95	2 36	62 63	24 42	10 59	100 0
2	36 83	1 95	58 29	23 57	16 19	100 0
3	42 40	2 73	59 24	24 98	14 50	101 5
4	25 22	1 67	57 98	27 83	11 90	99 4
5	28 38	3 11	64 63	14 38	17 30	99 4
6	25 38	4 12	69 53	12 06	13 79	99 5
7	31 24	4 04	67 33	13 74	14 89	100 0

* Experiments 1 4 were carried out using benzene as solvent for sulphur nitride, whereas dioxan was used as solvent for experiments 5 7

† Quantities of sulphur and sulphur compounds are all expressed in terms of gramme atoms of sulphur 10^4

---

(3) A WEISSBERGER, *Organic Solvents* Interscience, New York (1955)

(4) I M KOLTHOFF and V A STENGER, *Volumetric Analysis*, Vol 1, p 161 Interscience, New York (1942)

(5) A KURTENACKER *Analytische Chemie der Sauerstoffsauren des Schwefels* Stuttgart (1938)

(6) M GOEHRING, U FELDMANN and W HELBING, *Z Analyt Chem* **129**, 346 (1939)

any blank correction in the case of alkaline and acid hydrolyses and the reaction with sodium sulphite In the case of the reaction with sodium thiosulphate in acid medium, it was found that blank corrections were necessary, this could be attributed to the probable decomposition of thiosulphuric acid during the reaction time

TABLE 2 —ACID HYDROLYSIS OF TETRASULPHUR TETRANITRIDE
(Over-all acidity 4 0 N)

Expt no *	Amount of sulphur nitride taken†	Hydrogen sulphide† (%)	Sulphur dioxide† (%)	Thiosulphate† (%)	Tetra-thionate† (%)	Elemental sulphur† (%)
1	30 96	3 67	77 50	1 65	3 29	13 89
2	45 44	7 79	71 48		—	20 73
3	38 27	4 95	69 31	—		25 74

* Benzene was used as solvent for sulphur nitride in expt No 1 and dioxan in expts no 2 and 3

† Quantities of sulphur and sulphur compounds are all expressed in terms of gramme atoms of sulphur 10^4

TABLE 3 —REACTION OF TETRASULPHUR TETRANITRIDE WITH SODIUM SULPHITE IN NEUTRAL MEDIUM

Expt no *	Sulphur nitride taken (M 10^4)	Sodium sulphite taken (M 10^4)	Sulphite unconsumed (M 10^4)	Sulphite used up (M 10^4)	Sulphite expected to be used up (M 10^4)	Trithionate formed (M 10^4)	Trithionate expected to be formed (M 10^4)
1	7 50	15 00	5 07	9 93	15 00	10 11	15 00
2	8 31	33 24	19 33	13 91	16 62	13 57	16 63
3	6 77	54 16	40 73	13 43	13 54	13 44	13 54
4	7 50	75 00	59 40	15 60	15 00	14 91	15 00
5	7 79	77 90	61 78	16 12	15 58	15 44	15 58

* Dioxan was used as solvent for sulphur nitride in expts 1 4 whereas benzene was used in expt 5

TABLE 4 —REACTION OF TETRASULPHUR TETRANITRIDE WITH SODIUM THIOSULPHATE IN ACETIC ACID MEDIUM
(Over-all acidity 0 60 N)

Expt no *	Sulphur nitride taken (M 10^4)	Thiosulphate taken (M 10^4)	Thiosulphate left over (M 10^4)	Sulphite formed (M 10^4)	Pentathionate formed (M 10^4)	Tetra-thionate formed (M 10^4)
1	5 31	42 48	1 06	2 64	11 45	10 38
2	6 51	52 08	—	3 60	13 30	15 97
3	4 09	52 08	7 72		13 84	8 91
4	nil	52 08	35 66	10 37	2 13	0 27

* Benzene was used as solvent for sulphur nitride in expt 1 and dioxan in expts 2 and 3 The blank expt 4 was carried out in a solvent mixture of the same composition as expts 2 and 3

RESULTS

Alkaline hydrolysis

Tetrasulphur tetranitride is quantitatively hydrolysed by alkali in a homogeneous medium The products of hydrolysis are sulphite, thiosulphate, sulphate and a small quantity of sulphite Using an over-all alkali strength of 0 50 N and benzene as *solvent for sulphur nitride it was found that nearly 60 per cent of the sulphur nitride was converted into sulphite (Table 1) About 23-28 per cent thiosulphate, 10-16 per* cent sulphate and 2-3 per cent of sulphide were also obtained When dioxan was used as solvent, the thiosulphate yield decreased to 12 14 per cent while sulphite yield increased to 65 70 per cent about 15 per cent sulphate and 3-4 per cent sulphide were also obtained Alkaline hydrolysis was complete in 2 hr, this was indicated by the gradual disappearance of the yellow colour of the sulphur nitride The solution remained clear throughout and became colourless at the end

Acid hydrolysis

Acid hydrolysis of sulphur nitride was found to be slower than alkali hydrolysis The hydrolysis was sluggish with dilute acid, but the reaction could be hastened by using an acidity of 4 N It may be seen from Table 2 that the main product of acid hydrolysis of sulphur nitride is sulphur dioxide Using benzene as solvent, about 78 per cent of sulphur dioxide, 14 per cent of elemental sulphur, 4 per cent of hydrogen sulphide and small quantities of thiosulphate and tetrathionate were obtained No thiosulphate or tetrathionate was obtained when dioxan was used as solvent, the sulphur dioxide yield was 70 per cent, elemental sulphur 20-25 per cent and hydrogen sulphide 5 8 per cent The absence of polythionates when dioxan was used as solvent could be attributed to the decomposition of polythionates to give elemental sulphur as shown by the increased yield of elemental sulphur in a dioxan solution

Reaction of sulphur nitride with sodium sulphite

It may be seen from Table 3 that sulphur nitride reacts with sodium sulphite in a neutral medium to give trithionate quantitatively A neutral medium was employed throughout this study since an acid medium would render the estimation of the unconsumed sulphite inaccurate and an alkine medium might cause the decomposition of the polythionates expected to be formed A known amount of a standard solution of sodium sulphite (stabilized by alcohol, 15 per cent by volume) was added and after about 30 min, the sulphite left unconsumed as well as the trithionate formed were estimated It was observed that a high concentration of sulphite was necessary for the reaction to be quantitative With a twofold or fourfold molar concentration of sulphite, trithionate yields were not quantitative, but when an eightfold or higher concentration of sulphite was employed, it was found that two moles of sulphite were consumed per mole of sulphur nitride to give two moles of trithionate The yellow colour of the sulphur nitride solution deepened to a transient red on the addition of sulphite and homogenization, the solution became colourless in less than 5 min when a large excess of sulphite was present No thiosulphate or higher polythionates were observed among the products

Reaction of sulphur nitride with thiosulphuric acid

The reaction of sulphur nitride with thiosulphate could be studied only in acid conditions since the higher polythionates expected to be formed would be decomposed in an alkaline solution The acid hydrolysis of sulphur nitride is, however, slow, also the acidity had to be kept low to minimize the decomposition of thiosulphate Acetic acid (0 60 N) was therefore employed

Sulphur nitride was completely consumed in about 1½-2 hr time using an eight to twelvefold molar concentration of thiosulphate The products are mainly pentathionate and tetrathionate (It may be seen from expt 4, Table 4, however, that thiosulphate itself, when left in a similar acid medium for 2 hrs, undergoes some conversion to pentathionate, sulphite and elemental sulphur)

The yellow colour of the sulphur nitride solution deepened to a red colour on the addition of thiosulphate and gradually faded and the solution became colourless after 1½–2 hrs

DISCUSSION

The constitution of sulphur nitride is discussed at length by GOEHRING(7), who suggests resonance between 8 canonical forms leading to the equivalence of all the N—S bonds The N—S bond length(8) in sulphur nitride is 1 60 Å, compared with the value of 1 74 Å for a N—S single bond and 1 54 Å for a N=S double bond, this indicates a partial double bond character for the N—S bond in sulphur nitride The interatomic distance between two sulphur atoms connected through a nitrogen atom is 2 71 Å and that between two sulphur atoms not connected through nitrogen is 2 58 Å This latter interatomic distance is much smaller than the Van Der Waals' distance of 3 7 Å although larger than the S—S single bond length of 2 1 Å While this short distance is explained as due to contributions from cross-bonded structures in resonance, it is clear that no S—S chemical bond in the conventional sense exists in sulphur nitride The absence of N—N bonds, established by X-ray analysis,(8) is supported by hydrolytic results where all the nitrogen is converted into ammonia (1) When sulphur nitride is allowed to react with anhydrous hydrogen iodide in non-aqueous solvents like carbon tetrachloride,(9) all the sulphur is reduced to hydrogen sulphide and the entire nitrogen is converted into ammonia as per the equation

$$S_4N_4 + 20HI \rightarrow 4H_2S + 4NH_3 + 10I_2 \qquad (1)$$

The oxidation state of sulphur in hydrogen sulphide is −2, in order to bring all the four sulphur atoms present in sulphur nitride to this state, twenty equivalents of reductant are consumed Therefore the average oxidation number of sulphur in sulphur nitride may be taken as +3 Further evidence for the +3 oxidation state of sulphur in sulphur nitride has been adduced by the present authors from oxidation studies using chloramine-T (10) In this reaction, all the sulphur is oxidized to sulphuric acid and all the nitrogen is converted to ammonia

$$S_4N_4 + 6(O) + 10H_2O \rightarrow 4H_2SO_4 + 4NH_3 \qquad (2)$$

The oxidation state of sulphur in sulphuric acid is +6, since twelve equivalents of oxidant are consumed to bring all the four sulphur atoms in sulphur nitride to this state, the average oxidation number of sulphur in sulphur nitride may be seen to be 3 This implies an oxidation state of −3 for nitrogen in sulphur nitride The fact that all the nitrogen is converted into ammonia in all these hydrolytic, reductive and oxidative reactions proves that the oxidation state of nitrogen is unaltered in these reactions The electropositive nature of sulphur in sulphur nitride is in agreement with Pauling's electro-negativity scale (N 3 0, S 2 5)

M BECKE GOEHRING, *Progress in Inorganic Chemistry*, Vol 1, p 208 Interscience, New York (1959)

D CLARK, *J Chem Soc* 1615 (1952)

A R VASUDEVA MURTHY, *Proc Indian Acad Sci* **37**, 25 (1953)

G R NAIR and A R V MURTHY, *Chem and Industr* (In press)

These observations are compatible with the results of hydrolytic reactions if we assume the formation of a derivative of S^{3+}, viz, "sulphur trihydroxide" $S(OH)_3$ as the primary product of hydrolysis Such a product will be extremely unstable and will have only a transient existence, being transformed into sulphoxylic acid (in which sulphur is in the +2 oxidation state) and sulphurous acid (where sulphur is in the +4 oxidation state)

$$\begin{aligned} S_4N_4 + 12H_2O &\rightarrow 4S(OH)_3 + 4NH_3 \\ &\downarrow \\ &2S(OH)_2 + 2S(OH)_4 \\ &\qquad\qquad\downarrow \\ &\qquad\qquad 2H_2SO_3 + 2H_2O \end{aligned} \tag{3}$$

Sulphoxylic acid itself, while not isolated in the pure state or in solution, is known to be a highly reactive species as seen from studies on its derivatives [11] The secondary reactions undergone by sulphoxylic acid explain the formation of the various products in the hydrolysis of sulphur nitride

Alkaline and acid hydrolyses

On the basis of reaction (3), one might expect 50 per cent of the sulphur in sulphur nitride to be converted into sulphurous acid, whereas the actual percentage of sulphurous acid (or sulphite) obtained in acid or alkaline hydrolyses is much higher (60 75 per cent) This can be attributed to the decomposition reactions of sulphoxylic acid leading to the formation, among other products, of extra sulphite Sulphoxylic acid is known to undergo the following reactions in an alkaline medium [1 12]

$$2H_2SO_2 \rightarrow H_2S_2O_3 + H_2O \tag{4}$$

$$2H_2SO_2 \rightarrow H_2S + H_2SO_4 \tag{5}$$

$$3H_2SO_2 \rightarrow H_2S + 2H_2SO_3 \tag{6}$$

Besides, sulphoxylic acid reacts with sulphurous acid to form trithionate [11]

$$H_2SO_2 + 2H_2SO_3 \rightarrow H_2S_3O_6 + 2H_2O \tag{7}$$

Trithionate is known to be hydrolysed in presence of alkali in two ways depending upon the alkali strength [13]

$$S_3O_6^{2-} + OH^- \rightarrow HSO_4^- + S_2O_3^{2-} \tag{8}$$

$$2S_3O_6^{2-} + 6OH^- \rightarrow S_2O_3^{2-} + 4SO_3^{2-} + 3H_2O \tag{9}$$

The absence of trithionate and the presence of sulphate among the products are explained by these hydrolytic reactions of trithionate All the products of alkaline hydrolysis are thus accounted for qualitatively in terms of reactions (4) to (9), these analytical results are not amenable to exact quantitative evaluation due to the large number of complicating secondary reactions involved It may be mentioned that GOEHRING[1] did not observe sulphide among hydrolytic products, although MEUWSEN,[14] who heated sulphur nitride with aqueous alkali, had noticed a small quantity of sulphide

While acid hydrolysis is much more complicated than alkaline hydrolysis, the primary reaction (3) may be supposed to take place It may be further supposed that sulphoxylic acid disproportionates according to Equation (6) which explains the formation of some hydrogen sulphide A part of the hydrogen sulphide and sulphur dioxide react with each other giving elemental sulphur and polythionates

---

[11] M GOEHRING, *Z Anorg Chem* **253**, 304 (1947)

[12] A R V MURTHY, *Proc Indian Acad Sci* **36**, 396 (1952)

[13] O FOSS, *Kjl Norsk Viden Selsk Skrift* No 2 p 5 (1945)

[14] A MEUWSEN, *Ber Dtsch Chem Ges* **62**, 1968 (1929)

Reaction with sulphite and thiosulphate

The sulphite ion ranks high in "thiophilicity"$^{(15)}$ and is known to be very active in nucleophilic attacks on elemental sulphur$^{(16\ 17)}$ and several sulphur compounds The sulphoxylic acid produced in reaction (3) is quantitatively converted into trithionate by the sulphite present in excess, as per reaction (7) This reaction is known to take place rapidly in a neutral medium$^{(11)}$ The net result of reactions (3) and (7) would be that one mole of sulphur nitride consumes two moles of sulphite to give two moles of trithionate

$$\begin{array}{l} S_4N_4 \rightarrow 2S(OH)_2 + 2H_2SO_3 \\ \qquad \downarrow 4H_2SO_3 \\ \quad 2H_2S_3O_6 \end{array} \qquad (10)$$

It may be seen from Table 3 that these predictions are verified by the experimental results when an excess of sulphite is employed An excess of sulphite is necessary in order to suppress the competitive side reactions, viz, decomposition reactions of sulphoxylic acid The present analytical results confirm the observations of GOEHRING$^{(1)}$

The following reaction may be expected to occur between thiosulphate and sulphur nitride

$$\begin{array}{l} S_4N_4 \rightarrow 2S(OH)_2 + 2H_2SO_3 \\ \qquad \downarrow 4H_2S_2O_3 \\ \quad 2H_2S_5O_6 \end{array} \qquad (11)$$

Pentathionate is thus expected to be the main product However, due to the sulphite degradation of pentathionate, which takes place to some extent in the weakly acid medium, tetrathionate is also to be expected

$$S_5O_6^{2-} + SO_3^{2-} \rightarrow S_4O_6^{2-} + S_2O_3^{2-} \qquad (12)$$

The source for this sulphite is reaction (3) itself The situation is further complicated due to the fact that thiosulphate itself, left in the acid medium for 1½–2 hr leads to the formation of some pentathionate While quantitative correlations could not be made due to these complicating factors, it may be noted that pentathionate and tetrathionate are the main products, as expected

The ring system in sulphur nitride is opened up in all these hydrolytic reactions Also, the fact that polythionates and other sulphur chain compounds are present among the hydrolytic products although there there is no S–S bond in sulphur nitride testifies to the marked tendency for the sulphur atoms to link with one another forming straight sulphur chain compounds, this tendency being especially strong in the presence of thiophilic reagents like sulphite and thiosulphate

---

W A PRYOR *Mechanisms of sulphur reactions*, p 60 McGraw-Hill, New York (1962)

M SCHMIDT and G TALSKY *Ber Chem Dtsch Ges* **90**, 1673 (1957)

R V MURTHY and V R S RAO; *J Sci and Industr Res* **18 B**, 40 (1959)

J Inorg Nucl Chem , 1963, Vol 25, pp 461 to 464 Pergamon Press Ltd Printed in Northern Ireland

NOTES

Ammonium uranates and UO_3-hydrates-ammoniates

(*Received* 16 *July* 1962)

IN PAST years we have found a distressing number of so-called ammonium uranates, all differing in their X-ray diagrams The situation being most confused, this contribution is intended to show that different series of compounds might occur in parallel, depending on the method of preparation

Several different crystalline products can be obtained by precipitation with urea from a homogeneous solution⁽¹⁾ A few years ago an attempt to identify these products led us to the conclusion that at least some ammonium uranates are, in fact, UO_3-hydrates-ammoniates with a general formula $UO_3 (2\text{-}x)H_2O\ xNH_3$

The reaction of gaseous or dissolved ammonia with a 0 15 to 0 60 molar uranyl nitrate solution at room temperature yielded, below pH = 9 5, three products, with distinctly different X-ray diagrams, indicating closely related orthorhombic lattices The products were designated α, β, and γ, with transition points at a pH around 3 and 9 respectively The transition $\beta \rightleftarrows \gamma$ was reversible in the mother liquor and was shown to depend solely on the pH, whereas under nitrate-free conditions the reaction $\gamma \rightarrow \beta$ seemed to be irreversible

The strong resemblance of the X-ray diagrams of the α, β, γ forms and that of $UO_3\ 2H_2O$ was closer than might be expected between ammonium uranates and $UO_3\ 2H_2O$ This suggested that ammonia replaced H_2O in the lattice as NH_3, instead of being present in the form of NH_4^+ as it would have been if the compounds were ammonium uranates This concept seems to be in agreement with infrared work carried out by DEANE⁽²⁾ and with an X-ray diffraction study by GARNER ⁽³⁾

For further experiments a reactive $UO_3\ 2H_2O$ was prepared by electrodialysis of the amorphous product from the urea process⁽¹⁾ This material was washed several times with dry, liquid ammonia and dried free from adsorbed liquid A compound with a hexagonal structure was obtained

A surprising effect observed was that a continuous shift of the diffraction lines occurred while the diffraction diagram was being obtained, in the direction of increasing lattice parameter This was attributed to a loss of NH_3 from the sample The action of dry ammonia gas gave a compound ε as upper limit of the hexagonal region, with parameters $a = 4\ 03$ Å and $c = 7\ 12$ Å, whereas washing with water resulted in a compound δ with $a = 4\ 09$ and $c = 7\ 50$ Å, probably corresponding to the lower limit of NH_3 content of that region In the latter case, strong lines of β were present

Chemical analysis of the compounds β, δ and ε revealed compositions of

$$UO_3\ \tfrac{5}{3}H_2O\ \tfrac{1}{3}NH_3 \qquad (\beta)$$

$$UO_3\ \tfrac{3}{2}H_2O\ \tfrac{1}{2}NH_3 \qquad (\delta)$$

$$UO_3\ \tfrac{4}{3}H_2O\ \tfrac{2}{3}NH_3 \qquad (\varepsilon)$$

A recent reinvestigation of the pure UO_3—H_2O—NH_3 system by CORDFUNKE⁽⁵⁾ gave essentially the same results with a slight difference, he found two different hexagonal structures with a two phase region in between, whereas our conclusion was that a continuous region exists with much wider limits δ and ε respectively Furthermore, CORDFUNKE⁽⁶⁾ states that his products are real ammonium uranates

Recently we started an investigation on the reaction between dry gaseous NH_3 and $UO_3\ 2H_2O$ powder at room temperature Although the results are still very preliminary, they are interesting enough to report them The same $UO_3\ 2H_2O$ preparation was used as in the former experiments Dry nitrogen with different percentages of NH_3 gas was conducted across a well stirred sample of $UO_3\ 2H_2O$ powder With NH_3 contents of the solid approximately between 1 0 and 1 7 per cent by

---

[1] P BRAUN (N V Philips, Eindhoven) Personal Communication (1959)

[2] A M DEANE, A E R E —R 3411 (1960)

[3] E V GARNER, *J Inorg Nucl Chem* , **21**, 380 (1961)

[4] M E A HERMANS, *Proc 2nd Geneva Conf* **7**, 39 (1958)

[5] E H P CORDFUNKE, *J Nucl Inorg Chem* , **24**, 303 (1962)

[6] E H P CORDFUNKE, Personal Communication (1961)

weight, a new orthorhombic compound (ζ) was obtained. At 1.7% NH_3 a trifling but definite shift of the lines was observed (diagram η) which did not change until well above 3 per cent NH_3. Then, a hexagonal compound somewhere between δ and ε was obtained. Further action of dry, pure NH_3 gas gave a hexagonal compound with an even smaller c parameter than ε: a = 4.03 Å and c = 7.07 Å. The NH_3 content was at that moment 4.2 per cent corresponding to a composition $(UO_3)(1.2H_2O)(0.8NH_3)$.

The whole picture seems to be very intricate and needs further investigation. It appears that different series of compounds are formed in liquid or dry systems and in the former case even different if nitrate is present or absent. Confusing though this seems, it might be understood from the fact that different types of $UO_3 \cdot 2H_2O$ exist, as was pointed out by DELL[7]. These types differ because part of the water may be present as hydroxylic groups attached to UO_2. It is clear that the exchangeability of water against NH_3 and the resulting structures may differ depending on the structure of the initial $UO_3 \cdot 2H_2O$. This again may depend on the presence of liquid water or on the previous history. The existence of ammoniates and ammonium uranates might well be understood on the same grounds.

A further complication of our experiments with gaseous NH_3 arises from the fact that dry NH_3 was used. Consequently no equilibrium was reached and even at extremely low NH_3 concentrations hexagonal compounds could be obtained by prolonged treatment. The presence of water vapour in the gas results in products with lower NH_3 contents. It seems unlikely that a total of two molecules of water plus ammonia per molecule of UO_3 is preserved under dry conditions, as one would expect that a compound $UO_3(2-x)H_2O \cdot xNH_3$ could exist only in equilibrium with one definite combination of H_2O and NH_3 gas pressures.

A gas-solid reaction was studied to find a suitable measure for the reactivity of different types of $UO_3 \cdot 2H_2O$. Large differences in reaction rate were observed.

A more elaborate account of the work described above will be published in due course.

Acknowledgement—The authors wish to thank Mr. H. J. PENNINGS for his assistance in the experimental work.

M. E. A. HERMANS
T. MARKESTEIN

N.V. KEMA, Arnhem,
Netherlands

---

[7] R. M. DELL, Personal Communication (1962).

[8] M. E. A. HERMANS, To be published as thesis at Delft Technological University.

Un nouveau dispositif générateur d'Iode 132

(*Received* 9 *July* 1962, *in revised form* 10 *October* 1962)

L'IODE 132 (2,3 h) est un produit de filiation du Tellure 132 (71 h) que l'on trouve dans les produits de fission de l'Uranium.

Diverses méthodes de séparation de l'Iode 132 a partir du Tellure de fission ont ete décrites dans la littérature.

Le dispositif generateur d'Iode 132 generalement employe utilise une méthode decrite par TUCKER[1]. Il consiste en une colonne de 10 g d'alumine (hauteur 3,5 cm, section 3 cm^2) sur laquelle on fixe le Tellure (Tellure 132 et Tellure entraineur inactif) sous forme de Tellurite.

Avec ce dispositif, il peut arriver qu'une quantite non negligeable de Tellure entraîneur soit eluée en même temps que l'Iode 132. De plus, l'elution de l'Iode 132 necessite un temps assez long si on le compare a la periode de l'isotope (environ 45 min d'elution).

On a donc étudie une modification a cette methode, afin de reduire les inconvenients cites. Des essais ont ete poursuivis visant a remplacer la colonne d'alumine de 10 g par une colonne de 5 g seulement, mais capable de fixer tout le Tellure par addition d'une certaine quantité de nitrate d'aluminium: on fait coprecipiter l'hydroxyde avec le Tellurite par addition d'ammoniaque.

Différents essais ont permis de mettre en evidence l'influence des parametres suivants:

le Tellure est d'autant mieux fixe sur le precipité d'alumine que la quantite de nitrate d'aluminium ajoutée est plus grande.

Par exemple: pour coprecipiter 20 mg de Tellure, 2 ml d'une solution de nitrate d'aluminium a 10% sont suffisants.

L'exces d'ammoniaque diminue l'adsorption du tellurite sur l'alumine.

L'influence de la quantité d'ammoniaque ajoutée est d'autant moins sensible que la quantité de nitrate d'aluminium ajoutée est plus grande.

En pratique on est limité dans l'addition de nitrate d'aluminium, car l'hydroxyde d'aluminium amorphe déposé sur le lit d'alumine ralentit considérablement le débit de la colonne.

DESCRIPTION DU MODE OPÉRATOIRE

Ainsi les meilleures conditions opératoires semblent être pour une colonne de 2,2 cm de diamètre et une épaisseur d'alumine de 2 cm (environ 5 g).

Alumine Merck d'après Brockmann.

Après dissolution de l'oxyde d'Uranium dans HCl concentré, addition de 20 mg de Tellure entraîneur en solution.

Précipitation du Tellure par le chlorhydrate d'hydrazine.

Redissolution du Tellure par HNO_3 concentré, addition de 2 ml de nitrate d'aluminium à 10%.

Neutralisation jusqu'à précipitation de l'hydroxyde d'aluminium.

Remise en solution par quelques gouttes d'acide.

Pendant ces opérations: passage sur la colonne de 10 ml d'ammoniaque N.

Fixation de la solution active.

Lavage de la colonne par $NH_4OH(N/100)$.

Cette méthode est actuellement utilisée au C.E.N. de Saclay, pour la préparation de l'Iode 132.

Département des Radioéléments
du C.E.N. de Saclay
Gif-sur-Yvette (Seine-et-Oise)
France

E. HATZOPOULOS

(1) WINSCHE W. E., STANG L. G. Jr., TUCKER W. D. "Production of iodine-132", *Nucleonics* **8**, 3 14-18 (1951).

Use of sulphamic acid for dissolving plutonium*

(*Received* 16 *August* 1962, *in revised form* 28 *December* 1962)

PLUTONIUM metal was found to dissolve readily in sulphamic acid and sulphamic-nitric acid mixtures. This observation is of practical significance in repurification of the metal since the dissolution in nitric acid is quite slow, and most of the agents that are effective in dissolving plutonium (such as halogen acids) are highly corrosive to stainless steel equipment. The use of 1.7 M sulphamic acid for plutonium dissolution has made possible the elimination of costly platinum-lined equipment which was required to contain the HNO_3-HF mixtures formerly used.

DISSOLUTION OF PLUTONIUM METAL

Composition of dissolvent (M)		Temperature (°C)	Time (min)	Max conc Pu attained (g/l)	% of Total Hydrogen Ion Consumed†
HNO_3	NH_2SO_3H				
5.7	0.0	25–30	60	0.7	0.2
5.7	0.3	40–102‡	14§	68	14
3.0	1.0	25–59	10§	46	14.5
0.0	1.7	25–40	60§	134	~100

---

* The information contained in this article was developed during the course of work under contract AT(07-2)-1 with the U.S. Atomic Energy Commission.

† Calculated on the basis of Pu dissolving as Pu(III), except for the case of 5.7 HNO_3 where the formation of Pu(IV) was assumed.

‡ Solution was heated initially to 40°C and dissolution was then allowed to proceed.

§ Time at which reaction ceased.

The dissolution of massive metal and of metal turnings in solutions of HNO_3, NH_2SO_3H, and their mixtures gave the results shown in the table. In these experiments an excess of plutonium metal was added to the solution of interest and dissolution was continued until the reaction ceased. Thus, the maximum concentration of plutonium attained in solution was a measure of the extent to which the reaction would proceed.

It is believed that the dissolution in the presence of sulphamic acid occurs according to the reaction, $Pu + 3H^+ \rightarrow Pu^{+3} + \frac{3}{2}H_2\uparrow$ and that the sulphamate ion promotes this reaction. The heat liberated by this reaction is $\Delta H_{298} = -141.9$ (kcal/mol Pu)[1]. Since the sulphamate ion is less stable[2] (decomposing to sulphate) as the temperature is increased, adequate cooling is needed to maintain a low temperature during dissolution. The presence of nitric acid during dissolution also reduces the stability of the sulphamate.[2]

Extensive experience in the dissolution of plutonium metal confirmed the preliminary observations, showing that

1. If the solutions were not adequately cooled during dissolution the reaction ceased abruptly as a result of decomposition of the sulphamate. Thus if the temperature of a starting solution of 5.7M HNO_3, 0.3M NH_2SO_3H exceeded 50°C the reaction ceased.
2. Small amounts of sludge were formed in most dissolutions made in 1.7M NH_2SO_3H, and much more sludge was formed if HNO_3 was also present. A sample of sludge from dissolution in 1.7M NH_2SO_3 contained 62.6 per cent Pu by weight, the sludge apparently is a mixture of plutonium oxide and plutonium sulphate. Sludge formed during rapid, incomplete dissolution of the metal may contain finely divided metallic particles which are pyrophoric when exposed to air.
3. With proper cooling to prevent decomposition of sulphamate (temperature maintained below 40°C), the reaction in 1.7M NH_2SO_3H proceeded to essentially complete exhaustion of the hydrogen ion with very little sludge formation.

W. J. JENKINS

Savannah River Laboratory
E. I. du Pont de Nemours & Co
Aiken, South Carolina

---

[1] L. BREWER *et al.*, *The Transuranium Elements* NNES, IV 14B, Part II, Paper 6.40, G. T. Seaborg and J. J. Katz (Editors) McGraw-Hill, New York (1949).

[2] L. F. AUDRIETH, M. SVEDA, H. H. SISLER, and M. J. BUTLER, *Chem. Rev.* 26, 49 (1940).

J Inorg Nucl Chem , 1963, Vol 25 pp 465 to 472 Pergamon Press Ltd Printed in Northern Ireland

FISSION OF ^{232}Th BY REACTOR NEUTRONS. MASS-YIELD CURVE

R H Iyer, C K Mathews, N Ravindran, K Rengan,
D V Singh, M V Ramaniah and H D Sharma
Radiochemistry and Isotope Division Atomic Energy Establishment, Trombay
Bombay-73

(*Received* 28 *September* 1962)

Abstract—Fission yields of thirty nuclides covering the mass region 77–156 have been determined for the fission of thorium-232 by neutrons from the swimming pool reactor "Apsara", using radiochemical techniques The mass-yield curve has the two familiar peaks at mass numbers 90 and 140 The maximum peak yield is about 8 per cent and minimum trough yield about 0 03 per cent The yield data indicate the presence of a small third peak in the symmetric region of the mass-yield curve The third peak is about 0 5 per cent of the total mass-yield curve, has a maximum to minimum ratio of about 2 4 and a half-width of about seventeen mass mumbers

The data obtained have been compared with similar data in literature The results are discussed in the light of two-mode-fission hypothesis

Low energy fission of heavy elements like uranium is predominantly asymmetric [(1)] The symmetric fission contribution increases with increasing energy[(2)] and becomes predominant over asymmetric fission at bombarding energies of about 100 MeV In the case of lighter elements like lead and bismuth, symmetric fission was found to be predominant at all energies [(3)] In the case of ^{226}Ra which is of intermediate mass, moderate energy protons[(4)] and deuterons[(5)] gave a triple-peaked mass-yield curve while helium ions gave the more usual double-peaked mass-yield curve It was, therefore, surmised by Fairhall[(6)] that a sudden change in the character of mass-distribution takes place as the compound nucleus undergoing fission changes from actinium to thorium More recent results of Cobble and co-workers[(7 8)] show that the helium-ion induced fission of even a heavy nucleus like ^{233}U gives a triple-peaked curve but ^{235}U and ^{238}U give only double-peaked curves

This paper describes the results of work done during 1960 and 1961 on the fission of ^{232}Th by neutrons from the swimming pool reactor "Apsara", undertaken to obtain the fission yields in detail, particularly in the trough region so that it might be possible to decide whether the mass-yield curve has a small third peak Such a possibility is not ruled out by the results of Turkevich and Niday[(9)] on the pile neutron fission of

---

[(1)] E K Hyde, Report UCRL-9036 (1960)

[(2)] R B Leachman, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva* 1958, Vol **15**, P/2467, United Nations (1958)

[(3)] A W Fairhall, *Phys Rev* **102**, 1335 (1956)

[(4)] R C Jensen and A W Fairhall, *Phys Rev* **109**, 942 (1958)

[(5)] R C Jensen and A W Fairhall, *Phys Rev* **118**, 771 (1960)

[(6)] A W Fairhall *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva* 1958, Vol **15**, P/667, United Nations (1958)

[(7)] R Gunnink and J W Cobble, *Phys Rev* **115**, 1247 (1959)

[(8)] L J Colby, M L Shoaf and J W Cobble, *Phys Rev* **121**, 1415 (1961)

[(9)] A Turkevich and J B Niday, *Phys Rev* **84**, 52 (1951)

^{232}Th or even by those of Turkevich *et al* (10) on the (Li + D)-neutron fission of ^{232}Th The results are interesting in view of the recent calculations by Newson(11) which show a third peak for the fission of ^{232}Th by 2 8 MeV neutrons

EXPERIMENTAL

A *Principle*

The "comparison method" was used for the determination of fission yields (12) Thorium and uranium targets were always irradiated simultaneously and the fission products under consideration were isolated from both ^{99}Mo was isolated in all cases and was used as internal standard Mounting and counting of the corresponding samples were done in the same way so that geometry, absorption and scattering corrections were the same for both the samples

Defining D as the ratio of the total activity A_X of any fission product X formed, to that of the total ^{99}Mo activity formed under the same conditions, and R as the ratio of D_{Th}, the D-value in thorium fission to D_{U}, the D-value in uranium fission we have

$$D_{\mathrm{Th}} = (A_X)\mathrm{Th}/(A_{\mathrm{Mo}})\mathrm{Th}, \quad D_{\mathrm{U}} = (A_X)\mathrm{U}/(A_{\mathrm{Mo}})\mathrm{U}$$

and

$$R_X = D_{\mathrm{Th}}/D_{\mathrm{U}}$$

The activity $A_X = Y_X \lambda_X f E_X$
where Y_X is the fission yield of the particular nuclide, λ_X its decay constant, f the total number of fission events taking place in the target and E_X the counting efficiency for the fission product Then

$$R = \frac{(Y_X \lambda_X f E_X)\mathrm{Th}}{(Y_{\mathrm{Mo}} \lambda_{\mathrm{Mo}} f E_{\mathrm{Mo}})\mathrm{Th}} \Big/ \frac{(Y_X' \lambda_X f' E_X)\mathrm{U}}{(Y_{\mathrm{Mo}}' \lambda_{\mathrm{Mo}} f' E_{\mathrm{Mo}})\mathrm{U}}$$

where the quantities with primes refer to uranium fission and those without primes to thorium fission

$$R = \frac{(Y_X/Y_{\mathrm{Mo}})\mathrm{Th}}{(Y_X'/Y_{\mathrm{Mo}}')\mathrm{U}}$$

$$Y_X = R Y_X'(Y_{\mathrm{Mo}}/Y_{\mathrm{Mo}}')$$

If $Y_{\mathrm{Mo}}/Y_{\mathrm{Mo}}'$ is arbitrarily set equal to 1, then $Y_X = R Y_X'$

The product of R and (Y_X') gives a relative value for the yield of X in thorium fission The absolute yield is obtained by normalising the area under the relative mass-yield curve to 200 per cent This method obviates the necessity of absolute counting, but is comparable in accuracy to other methods

B *Irradiations*

Pure thorium oxide or thorium hydrocarbonate obtained from Messrs Indian Rare Earths Limited, and thorium and uranium metal foils obtained from the Metallurgy Division, Atomic Energy Establishment, Trombay, were used for the irradiations (Analyses of thorium samples showed that they contain 0 5 p p m of uranium, 0 8 p p m of cerium, 0 2 p p m of samarium and 0 08 p p m of iron) About 10 g of thorium oxide and about 0 5 g of uranium were used for each irradiation The samples were enclosed in separate pure aluminium foils in a water-tight aluminium container and placed in a fixed position in the core of "Apsara" reactor so that irradiations with the same neutron spectrum were obtained The duration of an irradiation varied from 15 min to 40 hr depending on the nuclides to be isolated During an irradiation, the power level of the reactor was maintained as steady as possible Small fluctuations in the power level during an irradiation do not affect the results significantly since both uranium and thorium were irradiated simultaneously in the same position

C *Dissolution*

After irradiation, the targets were separately dissolved in nitric or hydrochloric acid with or without carrier depending on the nuclides to be isolated Thorium targets required refluxing with acid

(10) A Turkevich, J B Niday and A Tompkins, *Phys Rev*, **89**, 552 (1953)

(11) H W Newson, *Phys Rev* **122**, 1224 (1961)

(12) R A Schmitt and N Sugarman, *Phys Rev* **95**, 1260 (1954)

generally with the addition of about 1 ml of 1 M hydrofluo-silicic acid. The vapours escaping during the dissolution were passed through an alkali trap which was later acidified and added to the main solution. Dissolution of the metal was vigorous and hence external cooling was necessary. With thorium oxide as well as thorium metal, a small amount of residue always remained undissolved and it had about 2 per cent of the ^{99}Mo activity. It was assumed that the distribution of all the fission products between the solution and the small amount of residue is the same since this had been checked previously when deutreon-irradiated thorium metal was dissolved.(13) The solutions were filtered through Whatman No. 42 filter and made up to a convenient volume.

Uranium metal dissolved easily in dilute nitric or hydrochloric acid. When hydrochloric acid was used hydrogen peroxide had to be added to dissolve the uranium oxide residue and also to oxidise uranium to uranyl state.

D. *General radiochemical procedure*

A known amount of inactive carrier was added to an aliquot of the solution and allowed to interchange with the fission product element of interest. After the interchange was complete, the element was separated and purified from the target material and other fission products and finally obtained as a precipitate for mounting. Standard radiochemical procedures(14–16) were used with appropriate modifications in the case of thorium targets to obtain the required purity from thorium, its daughter products and protactinium which is formed in quite large quantities.

E. *Mounting*

The precipitates were filtered through No. 42 filter (1 in. diameter) using a perspex filter stick. They were washed, dried and weighed along with the filter paper and centred on aluminium plates with double-coated cellulose tape and covered with cellophane paper of thickness about 3 mg/cm^2.

F. *Counting*

β- activites were assayed using Sugarman-type methane flow proportional counters having 1 in. diameter end windows covered with aluminised mylar of thickness about 1·1 mg/cm^2 and 2-mil stainless steel wire anodes. γ- activites were assayed using a 1·5 in × 1 in NaI(Tl) crystal in conjunction with a single channel or a hundred channel pulse height analyser. All samples were counted each time, long enough to keep statistical errors below 1 per cent. Wherever possible samples were counted till decay was complete.

G. *Calculation*

The *D*-values and *R*-values were calculated from counting data. The activity in cpm of any particular nuclide was read from the decay curve and corrected for aliquot, chemical yield and for decay after irradiation. Corrections for decay during irradiation cancelled out since uranium and thorium targets were always irradiated simultaneously, and this implies the assumption that the genetics of the nuclides considered are the same in the thermal fission of ^{235}U and in the fast neutron fission of ^{232}Th.

H. *Errors*†

Of the various factors that contribute to the errors in the fission yields reported here, the one associated with the selection of ^{235}U (n_{th}, f) yields is probably the most important. The values recommended by KATCOFF(17) have been used in this work and they are accurate to about

---

† The errors associated with the yield values in the trough region are discussed under 'Results and Discussion'.

M. V. RAMANIAH, Ph.D. Dissertation, Washington University, St. Louis (1956).

C. D. CORYELL and N. SUGARMAN (Editors), *Radiochemical Studies: The Fission Products* N.N.E.S., Div. IV, Vol. 9, McGraw-Hill, New York (1951).

J. KLEINBERG, Report LA-1721 (1954).

M. LINDNER, Report UCRL-4377 (1954).

S. KATCOFF, *Nucleonics*, **18**, No. 11, 201 (1960).

10 20 per cent, although some of them have much less uncertainty Also, the uncertainties in the trough region may be more than those in other regions Obviously, thorium fission yields, reported here, in any case cannot be more accurate than the ^{235}U fission yields

Errors arising from the differences in sizes and weights of precipitates between uranium and thorium runs are minimized by confining the precipitates to the same area and applying corrections for self-absorption and scattering wherever necessary

The error involved in the assumption that the genetic relationships in ^{232}Th (n_f, f) and ^{235}U (n_{th}, f) are the same is negligible since under the conditions of the experiments the isomer ratios in thorium fission are not expected to be different from that in uranium fission

The small fast fission contribution of ^{238}U (about 1 per cent of the ^{235}U fissions) would make the trough yields in thorium fission, at the most, about 5 per cent lower than the actual values Calculations based on equal charge displacement hypothesis[18] as well as the empirical Zp values of Wahl[19] indicate that the error introduced by way of the higher isobars of any nuclide isolated having appreciable independent yields, is not very serious

The contribution of thorium fission by the secondary neutrons inside the largest thorium target used is estimated to be less than 1 per cent of the primary fissions and therefore there cannot be any distortion of the mass distribution due to the secondary fission, particularly in view of the fact that the energy spectrum of the neutrons causing primary fission is not very different from the energy spectrum of the secondary neutrons

Another source of error is the normalization process in which it is assumed that the mass-yield curve is smooth and the total yield is 200 per cent

No corrections have been applied to the fission yields for the effects of neutron capture

The standard deviations of the *R*-values given in Table 1 give a measure of the systematic experimental errors but not those mentioned above The overall reliability of the values may be taken to be 10-20 per cent although the internal consistency of individual values may be much better

RESULTS AND DISCUSSION

Fission yields of thirty nuclides covering the mass range 77–156 were determined in the fission of ^{232}Th by neutrons from the swimming pool reactor "Apsara" The results are given in Table 1 The mass-yield curve drawn through the experimental points is shown in Fig 1 For comparison, the data of TURKEVICH and NIDAY[9] on the pile neutron fission of ^{232}Th are also included in the figure As can be seen from the curve, there is general agreement between the two sets of results, except for notable differences in the yields of ^{77}As, ^{105}Rh, ^{137}Cs and ^{140}Ba Further, additional data were obtained in the present investigation in the trough and heavy wing regions

The mass-yield curve has the two familiar peaks at mass numbers 90 and 140, each having a half-width of about fourteen mass numbers The maximum peak yield is about 8 per cent and the minimum trough yield is about 0 03 per cent As in the fission of uranium and other heavy elements, the position of the heavy peak remains unchanged

The yield of ^{105}Rh is only about 40 per cent of that reported by TURKEVICH and NIDAY The yields of ^{123}Sn and ^{125}Sn (which were not reported by TURKEVICH and NIDAY) are also quite low There is a progressive increase in the yields from mass number 105 reaching a maximum around mass number 115 and then there is a decrease in the yields, reaching a minimum at mass number 125 This trend of the yields gives rise to a small third peak in the trough region This is also in fair agreement with NEWSON's calculated mass-yield curve for the fission of ^{232}Th by 2 8 MeV neutrons[11] as illustrated in Fig 2 The third peak is quite narrow having a half-width of about 17 mass numbers similar to that of the single peak obtained in the 22-Mev deuteron fission of ^{209}Bi[3] and also the central peaks of the three-peaked mass-yield

---

[18] L E GLENDENIN, MIT Report No 35 (1949)

[19] A C WAHL, *J Inorg Nucl Chem*, **6**, 263 (1956)

TABLE 1.—FISSION YIELDS OF ^{232}Th

Nuclide	No. of determinations	R-value	Chain yield ^{235}U(n_{th},f)(%)	Yield ^{232}Th(n_f, f)(%)
^{77}As	3	2.83 ± 0.14	0.0083	0.011 ± 0.0006
^{83}Br	3	8.21 ± 0.59	0.51	1.92 ± 0.14
^{90}Sr	2	2.8 ± 0.10	5.77	7.41 ± 0.27
^{91}Sr	4	2.55 ± 0.20	5.81	6.80 ± 0.55
^{95}Zr	2	1.81 ± 0.11	6.2	5.15 ± 0.31
^{97}Zr	2	1.56 ± 0.02	5.9	4.22 ± 0.06
^{99}Mo		1.00	6.06	2.78
^{103}Ru	3	0.11 ± 0.005	3.0	0.15 ± 0.007
^{105}Rh	2	0.072 ± 0.003	0.9	0.030 ± 0.0014
^{106}Ru	3	0.23 ± 0.012	0.38	0.040 ± 0.0021
^{109}Pd	3	3.71 ± 0.28	0.03	0.051 ± 0.004
^{111}Ag	3	7.7 ± 0.7	0.019	0.067 ± 0.006
^{112}Pd	2	14.1 ± 1.3	0.01	0.065 ± 0.006
^{113}Ag	3	11.65 ± 0.85	0.011	0.059 ± 0.004
^{115}Cd	4	11.6 ± 0.6	0.0097	0.057 ± 0.004*
^{115m}Cd	4	16.3 ± 4.3	0.0007	
^{117}In	2	10.44 ± 1.22	0.011	0.053 ± 0.006
^{121}Sn	2	8.77 ± 0.40	0.015	0.060 ± 0.003
^{123}Sn	2	4.19 ± 0.18	0.015	0.029 ± 0.0012
^{125}Sn	3	2.7 ± 0.27	0.021	0.026 ± 0.002
^{127}Sb	4	1.52 ± 0.07	0.13	0.091 ± 0.004
^{131}I	3	1.22 ± 0.05	3.1	1.73 ± 0.07
^{137}Cs	2	1.58 ± 0.02	6.15	4.46 ± 0.06
^{139}Ba	3	2.21 ± 0.11	5.55	6.64 ± 0.033
^{140}Ba	5	2.92 ± 0.08	6.35	8.50 ± 0.23
^{141}Ce	2	2.86 ± 0.13	6.00	7.87 ± 0.36
^{143}Pr	4	2.66 ± 0.09	6.00	7.32 ± 0.25
^{144}Ce	2	2.88 ± 0.01	6.00	7.93 ± 0.03
^{147}Nd	4	3.08 ± 0.16	2.7	3.82 ± 0.20
^{149}Pm	1	1.82	1.13	0.945
^{156}Eu	2	0.410 ± 0.051	0.014	0.0027 ± 0.0003

*Total of ^{115}Cd 0.052 ± 0.002 and ^{115m}Cd 0.0052 ± 0.0014

curves in the fission of ^{226}Ra by 11 MeV protons$^{(1)}$ and 14.5 and 21.5 MeV deuterons.$^{(5)}$ The area under the third peak is about 0.5 per cent of the total area under the mass-yield curve and the ratio of the maximum to minimum yields is about 2.4.

A critical analysis of the reliability of the yield values in the trough region (mass numbers 105–125) is necessary to see whether the indicated small third peak is real. Of the nuclides investigated in this region, ^{105}Rh, ^{106}Ru, ^{109}Pd and ^{112}Pd[†] have simple decay schemes. The fission yields of these nuclides are therefore free from any uncertainties arising from their decay schemes. The other nuclides ^{111}Ag, ^{113}Ag, ^{115}Cd, ^{117}In, ^{121}Sn, ^{123}Sn and ^{125}Sn have complicated decay schemes and/or existence of isometric states. Of these, ^{111}Ag, ^{113}Ag and ^{115}Cd are formed almost completely by the decay of their short-lived parents. Since these nuclides are near the end of their respective decay chains, the uncertainties, if any, in the fission yields of these mass numbers will

---

[†] The R-value obtained for ^{112}Ag was about 20 per cent lower than that obtained for ^{112}Pd. The reason for this is not known.

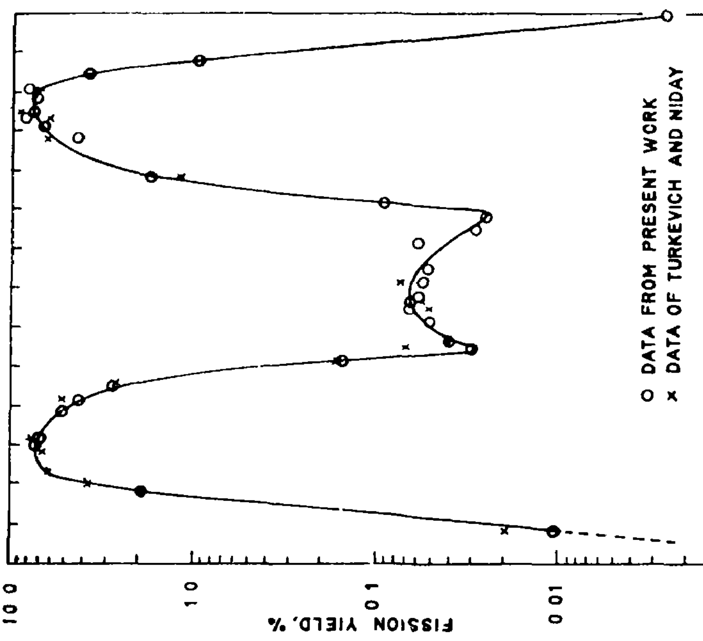

FISSION YIELD, %
10 0
1 0
0 1
0 01
0 001
MASS NUMBER
72
84
96
108
120
132
144
156
o DATA FROM PRESENT WORK
x DATA OF TURKEVICH AND NIDAY

FIG 1

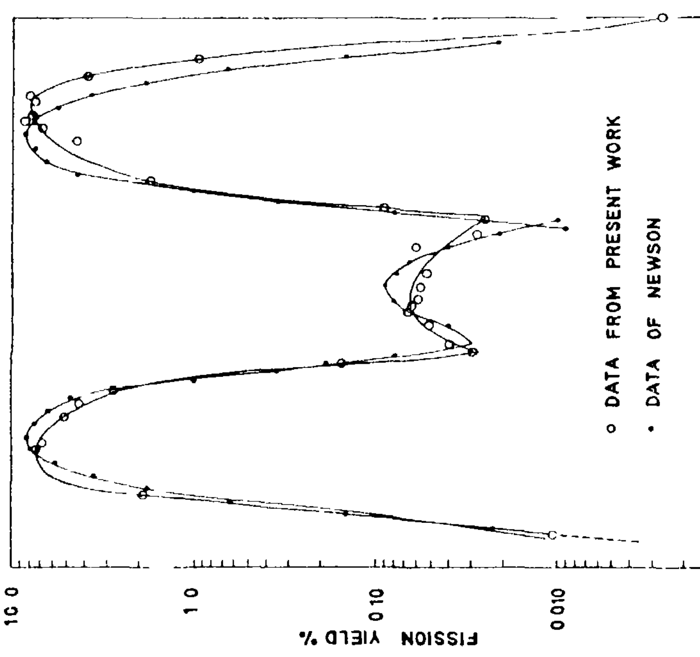

FISSION YIELD %
10 0
1 0
0 10
0 010
0 001
MASS NUMBER
72
84
96
108
120
132
144
156
o DATA FROM PRESENT WORK
• DATA OF NEWSON

FIG 2

be negligibly low. All the tin isotopes of our interest here exhibit nuclear isomerism. From the reported decay schemes(20) and yields for $^{235}U(n_{th}, f)$,(17, 20) it is clear that ^{121}Sn represents almost the total chain yield, while ^{123}Sn and ^{125}Sn represent only about 10 per cent and 60 per cent respectively of their total chain yields, the rest being accounted for, presumably, by the isomers. Since it was not possible to determine the yields of ^{123m}Sn and ^{125m}Sn due to their short half-lives (40 min and 9.5 min respectively), the yields of these mass numbers have some uncertainties. The independent yield of ^{123}Sn calculated on the basis of equal charge displacement hypothesis is only about 1.2 per cent and less than 1 per cent (0.06 per cent, $\bar{\nu} = 3$ or 0.01 per cent, $\bar{\nu} = 2$) of the total chain yield in ^{235}U and ^{232}Th fission respectively. This indicates that ^{123}Sn is formed almost completely by the beta decay of the unknown ^{123}In and the same fraction of the total activity, decided by the branching of the indium nuclide, is measured in both cases and hence the error in the *R*-value is expected to be low. In the case of ^{125}Sn, the fractional chain yield, calculated in the same way, is about 5 per cent ($\bar{\nu} = 3$) or 2 per cent ($\bar{\nu} = 2$) in ^{232}Th fission compared to about 11 per cent in ^{235}U fission. Taking the two extreme cases of the independently-formed tin forming entirely as ^{125m}Sn or ^{125}Sn, our result for the yield of mass number 125 using the value 0.021 for the chain yield of 125 in ^{235}U fission will be higher by about 8–10 per cent or lower by 3–5 per cent than the actual value. The *R*-value obtained from ^{125}Sb activity is actually a little lower than that obtained from ^{125}Sn activity. This may be due to the very low counting rates of ^{125}Sb, particularly in the samples obtained from thorium fission. Reference should be made here to the recent suggestion of WAHL and co-workers(19, 21) that in low energy fission, fifty-proton fragment formation is favoured. If this is the case, the equal charge displacement hypothesis is not valid in the symmetric fission region, and the errors in the values of tin nuclides could be much larger (or even smaller) than mentioned above. However, this effect makes the yields of the nuclides of elements from rhodium to indium more secure from the errors due to the differences in the independent yields in uranium and thorium fissions, as these nuclides are then preferentially formed by the decay of precursors far removed from them (forty-two-proton molybdenum etc. in uranium fission and forty-proton zirconium etc. in thorium fission).

From the above considerations, the third peak in the mass-yield curve may be taken to be real, although one would like to have data free from the uncertainties mentioned earlier. This triple-peaked mass distribution is one of the few such cases reported so far. FAIRHALL and JENSEN were the first to obtain a triple-peaked mass-yield curve in the fission of ^{226}Ra by 11 MeV protons.(4) This was followed by their observation of a triple-peaked mass-distribution in the 14.5 and 21.5 MeV deuteron fission of ^{225}Ra.(5) Fission of ^{226}Ra by 20 and 30 MeV helium ions, however, was found to give the more usual double-peaked curves. FAIRHALL explained his results on the basis of the two-mode fission hypothesis, first suggested by TURKEVICH and NIDAY(9), the triple-peaked curve resulting from the superposition of a double-peaked one due to asymmetric fission, and a narrow single-peaked one, similar in shape and width to that obtained in the 22 MeV deuteron fission of ^{209}Bi,(3) due to symmetric fission. The non-existence of a third peak in the helium-ion induced fission of ^{226}Ra

P STEINBERG and L E GLENDENIN, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva* 1956, Vol. 7, P/614. United Nations (1957).

A C WAHL, R L FERGUSON, D R NETHAWAY, D F TROUTNER and K WOLFSBERG, *Phys. Rev.* 126, 1112 (1962).

was then attributed to a sharp difference between the fission of thorium compound nuclei and actinium compound nuclei(6) If the triple-peaked curve in the present case is the result of superposition of symmetric and asymmetric curves, it provides additional evidence for the validity of this hypothesis in the heavy element region However, it is not clear why in the work of COBBLE and co-workers the helium-ion induced fission of ^{233}U(8) only should show such a distribution but not ^{235}U and ^{238}U(7 8) Similarly, it is not clear why the fission of other heavy nuclei by particles in the energy range of 30- 40 MeV(22) does not yield three-peaked mass distribution It appears that a clear understanding as to whether the triple-peaked mass distribution is due to superposition of the two modes or it is inherent in the fission of a nucleus under a set of conditions of Z, A and E^*, has to await a more thorough investigation, particularly in the heavy element region It must be added here that the variation of the number of neutrons emitted as a function of the fragment mass, with its sharp discontinuity at half the mass number of the compound nucleus, as observed by Whetstone in the spontaneous fission of ^{252}Cf(23) may be one of the factors responsible for the third peak observed in thorium fission

Acknowledgements --The authors are indebted to Dr G A WELCH for his keen interest in the work and for his helpful criticisms, to Professors A W FAIRHALL, N SUGARMAN and A C WAHL for their helpful comments and suggestions for the preparation of this paper and to Professor H W NEWSON for his interest in the work They are also thankful to Mr M N NAMBOODIRI for his help

E^* stands for the excitation energy of the compound nucleus

(22) R A GLASS, R J CARR, J W COBBLE and G T SEABORG, *Phys Rev* **104,** 434 (1956)

(23) S L WHETSTONE, *Phys Rev* **114,** 581 (1959)

J Inorg Nucl Chem 1963, Vol 25 pp 473 to 481 Pergamon Press Ltd Printed in Northern Ireland

α-ANNEALING OF NUCLEAR RECOIL ATOMS

P N DIMOTAKIS and M I STAMOULI
Chemistry Division, Nuclear Research Centre Democritus, Athens, Greece

(*Received* 10 *September* 1962, *in revised form* 22 *October* 1962)

Abstract The effect of α-particle bombardment on the retention phenomena in a neutron irradiated cobalt complex was examined α-Particles were produced in the solid system from the $^{10}B(n, \alpha)^7Li$ reaction, occurring in mixtures of the complex with boric acid or ammonium hydrogen tetraborate An increase in the retention of ^{60}Co in these mixtures was observed, depending on the dose of recoil α-particles and ^7Li atoms (from 10 to 83 Mrads) The kinetics of the isothermal annealing of these mixtures were also examined

THE annealing of nuclear recoil damage in solid materials was first reported by WILLIAMS(1) who noticed that the specific activity of radioactive antimony produced by the reactor irradiation of ammonium fluoantimonate and antimony pentafluoride decreased with increasing time of irradiation Williams ascribed this decrease in initially separable antimony atoms to an increase in retention with time of irradiation Radiation annealing was also observed on exposing these neutron irradiated substances to ionizing radiation

Thermal annealing was subsequently found by GREEN and MADDOCK(2) in potassium chromate—the retention of ^{51}Cr in this salt could be increased by heating the neutron-irradiated crystals Radiation and especially thermal annealing have since been observed in many systems

Photo-annealing in neutron irradiated phosphates was recently reported by CLARIDGE and MADDOCK(3) who used a mercury-vapour lamp giving a high dose of ultra-violet photons

Radiation annealing can also be achieved by X-rays and β-particles Because of the low penetration of β-particles the material to be irradiated must be prepared in thin layers

No annealing by α-particles has yet been reported These particles are easily absorbed in the surface of a solid material due to their extremely high specific ionization

In order to examine the α-particle effect on the recoil phenomena in neutron irradiated material, we have used an α-particle producing nuclear reaction, taking place in the solid system

The $^{10}B(n, \alpha)^7Li$ reaction was chosen as suitable This can be arranged by mixing a boron compound with the material and subjecting the whole system to neutron irradiation

---

R WILLIAMS, *J Phys Colloid Chem* **52**, 603 (1948)

H GREEN and A G MADDOCK, *Nature, Lond* **164**, 788 (1949)

R I C CLARIDGE and A G MADDOCK, *Symposium on Chemical Effects of Nuclear Transformations*, IAEA, Prague, October (1960)

EXPERIMENTAL AND RESULTS

(a) *Materials*

The material to be examined was trisethylenediamine cobalt(III) nitrate $[Co(en)_3](NO_3)_3$ which was prepared from reagents of analytical purity using the procedure of J B WORK(4) The boron compounds were *boric acid* H_3BO_3 *and hydrogen ammonium tetraborate* $NH_4HB_4O_7\,4H_2O$, *both of analytical purity*

(b) *Sample preparation*

The cobalt complex boron compound mixtures were prepared either by mixing and grinding or by preparing a pellet of the finely powdered mixed constituents under a pressure of 270 atm for 5 min after a vacuum had been applied for about 10 min

(c) *Irradiation*

The samples were irradiated in polythene tubes at the EL-3 reactor at Saclay CEA in a thermal neutron flux 1 10^{11} n/cm^2 sec for 2 and 3 25 hours and 1 2 10^{11} n/cm^2 sec for 21 hours

(d) *Method of analysis*

The ionic cobalt-60 and the ^{60}Co in the form of the parent complex were separated by an ion exchange technique A Dowex-50   8 100/200 mesh cation exchange resin was used An irradiated sample of 1–2 mg was dissolved in water and some complex and ionic cobalt carrier were added The solution was passed through the column (2 5 cm long and 0 8 cm dia) and both ions $[Co(en)_3]^{3+}$ and Co^{2+} were absorbed in the upper part of the column The ionic cobalt was first eluted by hydrochloric acid solution (1 2 N), the eluant being collected in a volumetric flask of 50 ml Then the complex was eluted by concentrated hydrochloric acid (1 1) and the eluant again collected in a 50 ml volumetric flask The two volumetric flasks were filled up to the mark with water and the radioactivity of the two separated constituents was measured by means of a single channel pulse-height analyser (Phillips)

(e) *Energy imparted to the crystalline complex due to the* ^{10}B(*n*, α)^{7}Li *nuclear reaction*

The energy *Q* of the exoergic nuclear reaction ^{10}B(n, α)^{7}Li is 2 793 MeV A proportion of 94 per cent of the reactions leaves the ^{7}Li nucleus in an excited state of 0 47 MeV above the ground state followed by a γ-transition(5) Thus the energy given to the products in the form of kinetic energy is 2 793 - 0 47 - 2 323 MeV and, taking into consideration the 6 per cent portion which gives the products 2 793 MeV, we can assume a mean value of 2 35 MeV imparted to the α-particle and ^{7}Li atom The distribution of this kinetic energy is 2 35   4/11   0 854 MeV for the ^{7}Li and 2 35   7/11 = 1 496 MeV for the α-particle Using these data and assuming that the whole of the kinetic energy is deposited in the crystals, the dose was calculated Thus for pellets containing 0 015 g boric acid and 0 285 g of the cobalt complex, an integrated thermal neutron flux of 7 2 10^{14} neutrons/cm^2 gave a dose of 9 83 Mrads In the same way all the other mixtures have been calculated

(f) *Initial retention*

The results for the initial retention of neutron irradiated samples are presented for three sets of experiments in Tables 1, 2 and 3

(g) *Isothermal annealing of neutron irradiated samples*

All the reactor irradiated samples, mixtures or complex alone, either in a pellet form or in powder have been examined as far as their isothermal annealing is concerned

Samples were heated at various temperatures in a thermostatically controlled oven (±0 5°C)

Fig 1 shows the isothermal annealing of the complex irradiated in a neutron flux of 10^{11} neutron/cm^2 sec for 2 hr in a pellet form Figure 2 shows the isothermal annealing of a mixture of (19 1)

---

(4) *Inorganic Syntheses*, Vol 2, W C FERNELIUS, McGraw-Hill, New York (1946)

(5) G C HANNA, *Phys Rev* **80**, 530 (1950)

TABLE 1

$\Phi = 10^{11}$ neutrons/cm² sec, time = 2 hr

Sample	Dose (Mrads)	Retention R(O) (%)	
		Pellet	Powder
Complex	0	40.1	37.8
Complex + $NH_4HB_4O_7$	10	50.5	—
Complex + H_3BO_3	10	43.4	41.4

TABLE 2

$\Phi = 1.2 \times 10^{11}$ neutrons/cm² sec, time = 21 hr

Sample	Dose (Mrads)	Retention R(O) (%) Pellet
Complex	0	63.4
Complex + $NH_4HB_4O_7$	83	67.3
Complex + H_3BO_3	83	58.2

TABLE 3

$\Phi = 10^{11}$ neutrons/cm² sec, time = 3.25′ hr

Sample	Dose (Mrads)	Retention R(O) (%) Pellet
Complex	0	50.7
Complex + $NH_4HB_4O_7$	10.7	56.2
Complex + $NH_4HB_4O_7$	21.4	65.8
Complex + $NH_4HB_4O_7$	32.1	55.5
Complex + $NH_4HB_4O_7$	42.8	52.5
Complex + $NH_4HB_4O_7$	64.2	54.7

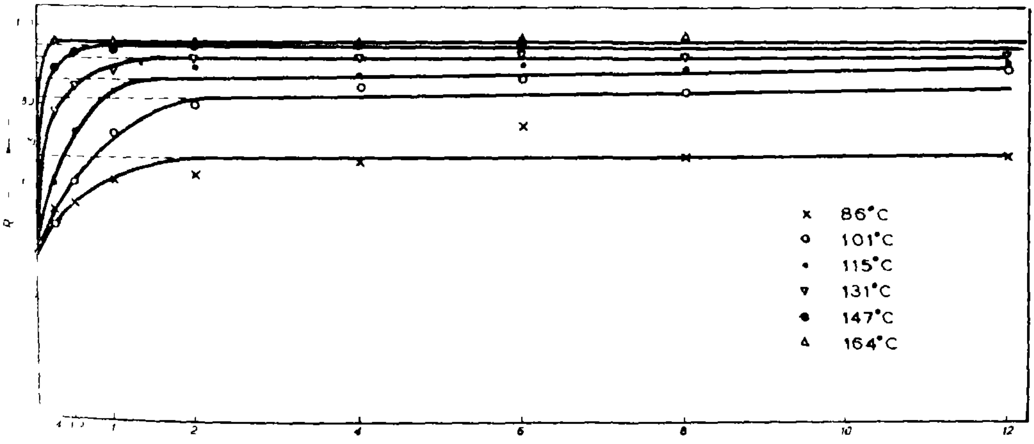


FIG. 1 – Isothermal annealing of neutron irradiated $[Co(en)_3](NO_3)_3$ in a pellet form Integrated flux 7.2×10^{14} neutrons/cm²

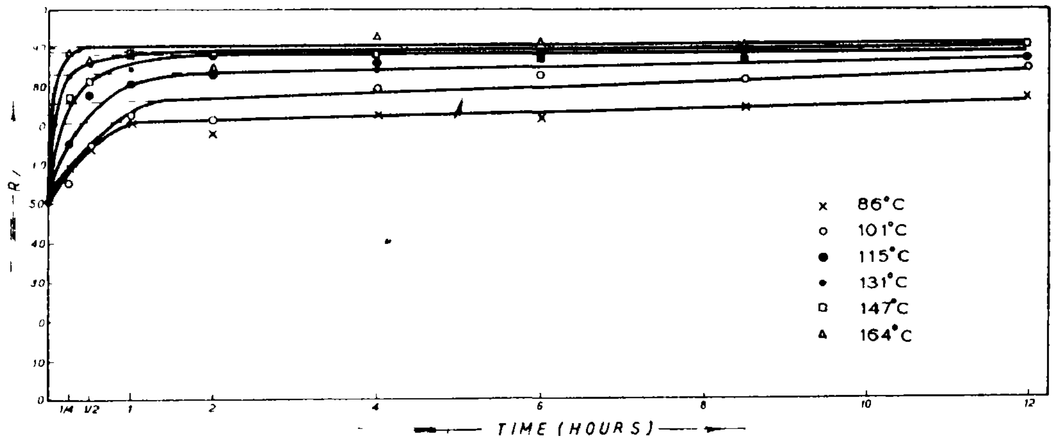


FIG 2 —Isothermal annealing of neutron irradiated mixture of (19 1) complex-tetraborate in a pellet form Integrated flux 7 2 × 10^{14} neutrons/cm² α, ^{7}Li dose ~10 Mrads

complex-tetraborate ratio in the same flux which gave 10 Mrads due to the (n, α) reaction of ^{10}B Also in Fig 3 the isothermal annealing of a mixture of (19 1) complex–boric acid ratio (~10 Mrads) is presented Figures 4 and 5 show the isothermal annealing in a powder form of the complex and in a mixture with boric acid (10 Mrads) respectively

In each case powder and pellet, the complex and the mixtures, with the exception of pellet with H_3BO_3, follow Maddock's law

$$\Delta R_e = C/T \quad S \qquad \text{(Fig 6)}$$

The isothermal annealing of the complex and mixtures (29 1) with tetraborate and boric acid in a high dose condition (~83 Mrads from the (n, α) reaction) and in a flux of 1 2 × 10^{11} neutrons/cm² sec are shown in Figs 7, 8, 9 respectively The same ΔR_e vs $1/T$ relation is found as can be seen from Fig 10

Isothermal annealing was also carried out on all the samples with different amount of tetraborate, thus giving 10 7, 21 4, 32 1, 42 8 and 64 2 Mrads doses

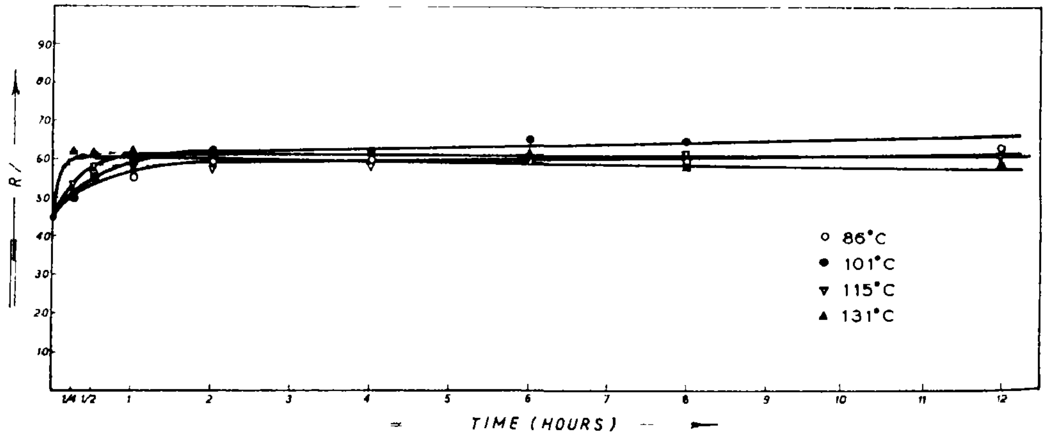


FIG 3 —Isothermal annealing of neutron irradiated mixture of (19 1) complex-boric acid in a pellet form Integrated flux 7 2 × 10^{14} neutrons/cm² α, ^{7}Li dose ~10 Mrads

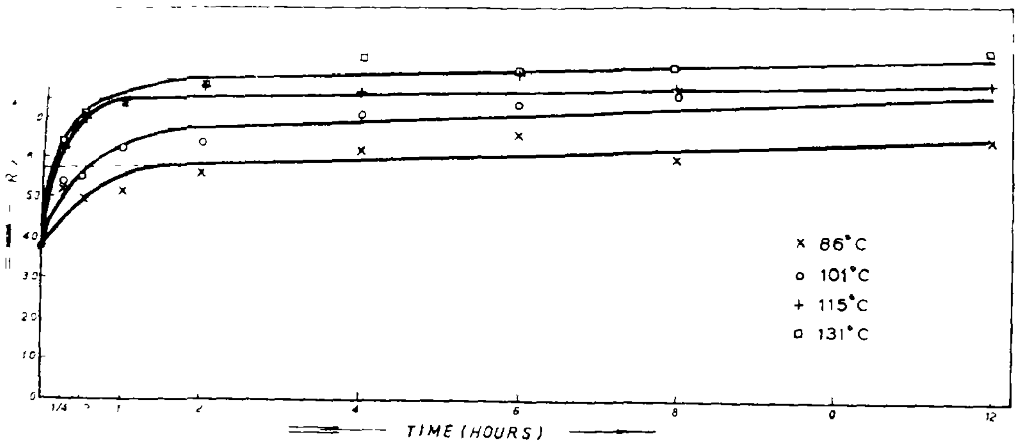


FIG 4 —Isothermal annealing of neutron irradiated $[Co(en)_3](NO_3)_3$ in a powder form Integrated flux 7 2 × 10^{14} neutrons/cm^2

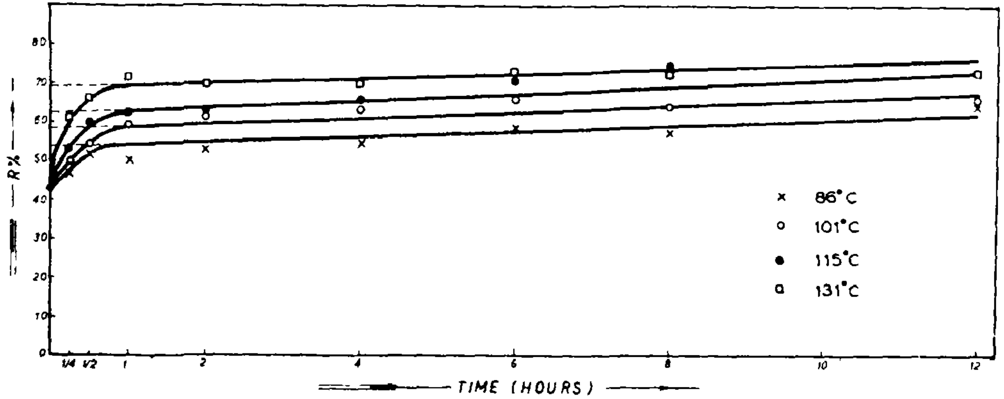


FIG 5 —Isothermal annealing of neutron irradiated mixture of (19 1) complex-boric acid in a powder form Integrated flux 7 2 × 10^{14} neutrons/cm^2 α, ^{7}Li dose ~10 Mrads

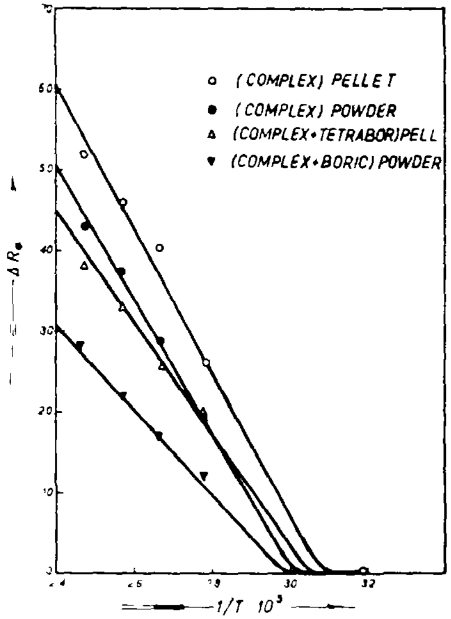


FIG 6 —ΔR_e plot versus $1/T$ for 7 2 × 10^{14} neutrons/cm^2 irradiated samples

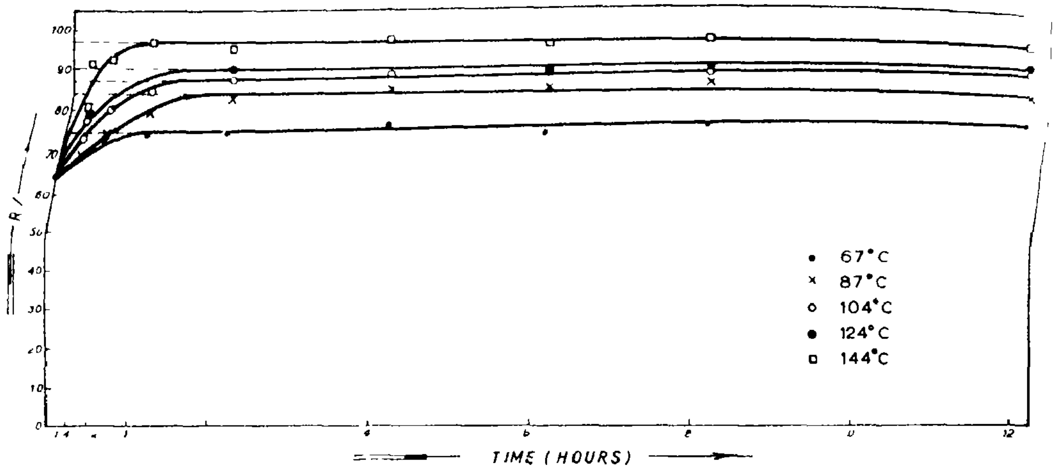


FIG. 7 Isothermal annealing of neutron irradiated $[Co(en)_3]$ $(NO_3)_3$ in pellet form Integrated flux 9 07 10^{15} neutrons/cm^2

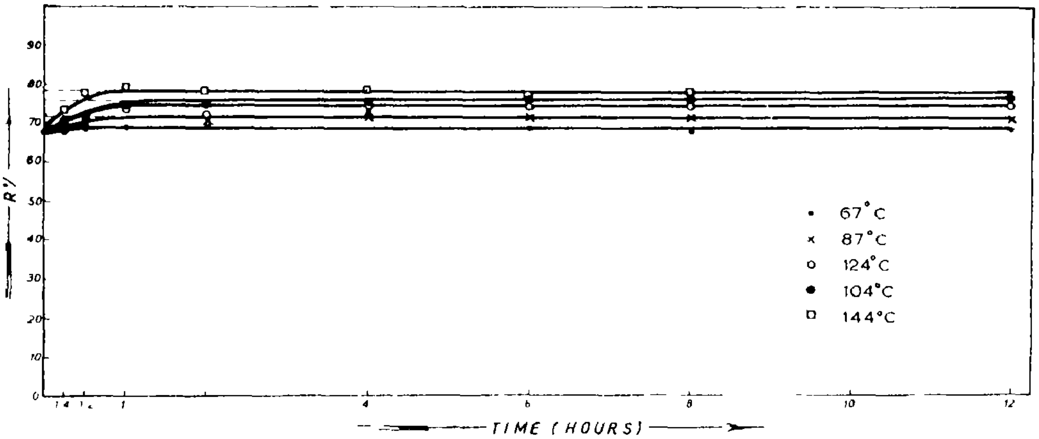


FIG. 8 Isothermal annealing of neutron irradiated mixture of (29 1) complex-tetraborate in a pellet form Integrated flux 9 07 10^{15} neutrons/cm^2 α, ^{7}Li dose ~83 Mrads

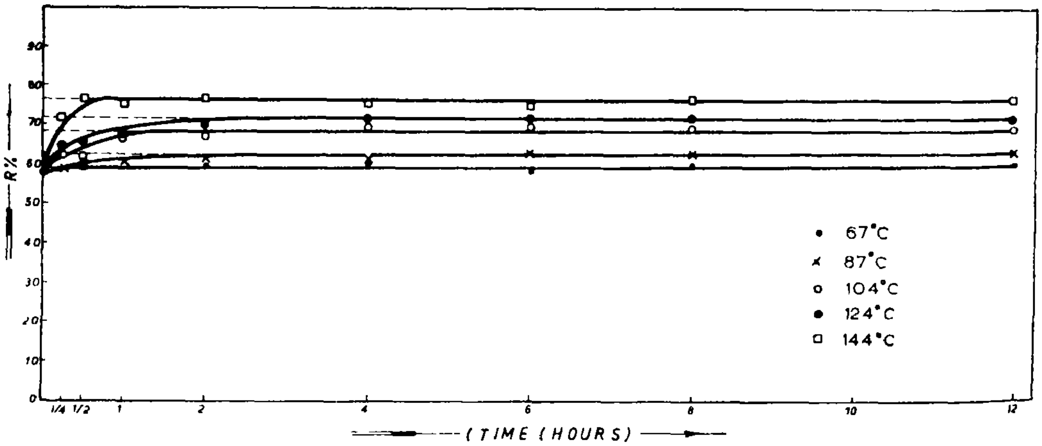


FIG 9 —Isothermal annealing of neutron irradiated mixture of (29 1) complex-boric acid in a pellet form Integrated flux 9 07 × 10^{15} neutrons/cm^2 α, ^{7}Li dose ~83 Mrads

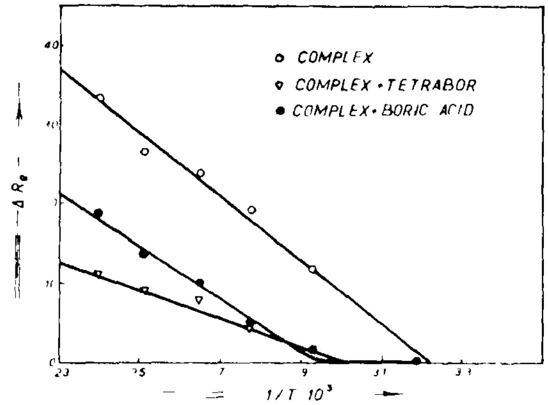


FIG 10 —ΔR_α plot versus $1/T$ for 9 07 10^{19} neutrons/cm² irradiated samples

DISCUSSION

Initial retention

The pellet preparation under pressure aimed at bringing into close contact the microcrystals of the complex and the tetraborate salt or the boric acid which were used as the source of internal α-irradiation of the complex For comparison samples were also irradiated in powder form with boric acid

The results of Table 1 show the difference in initial retentions, these being 40 1 and 37 8 per cent respectively, of the pure complex in a pellet and in a powder form The difference is due to the fact that, in the case of the powder some recoil atoms of ^{60}Co may leave the lattice of the microcrystals and lose the chance of being annealed afterwards This state of affairs is of negligible importance in the case of pellets In a mixture with boric acid (~10 Mrads) in pellet and powder form, the retention was increased by the same amount, that is ΔR_α = 3 3 and 3 6 per cent respectively In a mixture with tetraborate salt (10 Mrads) the increase was ΔR_α = 10 4 per cent

In the case of extended neutron irradiation (Table 2) where the amount of tetraborate salt or boric acid gave a high dose (~83 Mrads) the retention of the pure complex was 63 4 while the tetraborate mixture gave 67 3 and the boric acid mixture 58 2 per cent This cannot be explained easily unless under these high doses radiolytic phenomena occur as well as some capture of recoil cobalt atoms into the various crystalline lattices of the two boron compounds This phenomenon may depend on the parameters of these lattices

In the third irradiation with 10 7, 21 4, 32 1, 42 8 and 64 2 Mrads dose from tetraborate salt, variation of initial retention with the dose was observed The highest was with 21 4 Mrads and the lowest with 42 8 Mrads (Table 4)

The ionizing radiation, concurrent with the neutron flux is approximately 0 5 Mrads per hour (EL-3 reactor), thus giving various increases of the retention, depending on the time of irradiation (Table 1, 2, 3)

By plotting the ΔR_α values i e the increase of retention versus the dose of α-particles and lithium-7 atoms (Fig 11), using data from the third irradiation (Table 3), a curve with a maximum at 21 4 Mrads and a minimum at 42 8 Mrads is obtained

The observed cases of increase of retention in the presence of the boron compounds

TABLE 4

Sample	Ratio	Integrated neutron flux (neutrons/cm²)	R(O) (%)	α, ⁷Li Dose (Mrads)	ΔR_α (%)
Complex		7.2×10^{14}	40.1	0	0
Complex + tetrabor	19:1	7.2×10^{14}	50.5	10	10.4
Complex	–	9.07×10^{15}	63.4	0	0
Complex + tetrabor	29:1	9.07×10^{15}	67.3	83	3.9
Complex		1.17×10^{16}	50.7	0	0
Complex + tetrabor	29:1	1.17×10^{16}	56.2	10.7	5.5
Complex + tetrabor	14:1	1.17×10^{16}	65.8	21.4	15.1
Complex + tetrabor	9:1	1.17×10^{16}	55.5	32.1	4.8
Complex + tetrabor	6.5:1	1.17×10^{16}	52.5	42.8	1.8
Complex + tetrabor	4:1	1.17×10^{16}	54.7	64.2	4.0

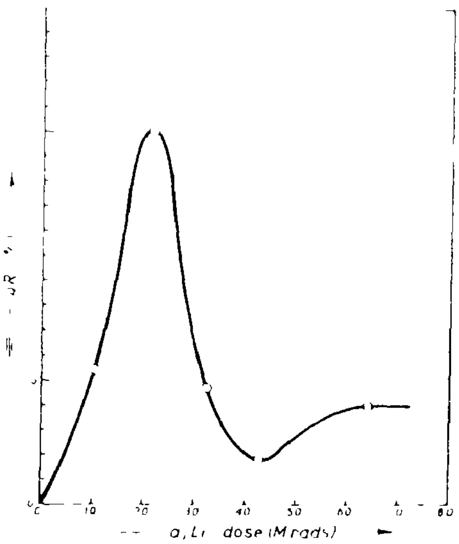


FIG. 11 – ΔR_α plot versus α, ⁷Li dose for the third set of irradiation

show that the (n, α) reaction in ^{10}B taking place during the production of the recoil phenomena imparts to the lattice of the complex enough energy to recombine an appreciable proportion of the recoil cobalt atoms

We have calculated the range into the solid complex of α-particles having the kinetic energy from the above reaction and it was found to be 4–5 μ [6]

There is no doubt that the energy of this nuclear reaction decreases the recombination activation energy of the recoil cobalt atoms through the same fundamental phenomena as in radiation and thermal annealing

Isothermal annealing

All the samples which were isothermally annealed showed the usual kinetics of a first order reaction plus a zero order slow linear annealing By comparing the ΔR values a decrease in the α, ^{7}Li annealed samples is always observed. This might be explained either on the basis of the radiolytic action of the α, ^{7}Li internal radiation or by a kind of capture by the boron compound lattice of the recoil cobalt atoms which have travelled very far within the solid material and consequently are annealed at higher temperatures The difference between the results in boric acid and tetraborate mixtures might be due to the different parameters of their crystalline lattices. Thus, recoil cobalt atoms passing through different boron compounds may be captured by them or the recombination conditions may change according to the nature of those crystal lattices

---

[6] G FRIEDLANDER and J KENNEDY *Nuclear and Radiochemistry* J Wiley, New York (1955)

General conclusion

The α-particle producing nuclear reaction ^{10}B(n, α)^{7}Li seems to increase the retention of the recoil cobalt atoms to a considerable extent It is intended to apply the same reaction to various systems especially to those in which radiolytic phenomena are less pronounced

Acknowledgement —The authors are indebted to Dr A G MADDOCK, University Chemical Laboratory, Cambridge, England for helpful dicsussion, to Mr D MARKETOS for helping in bibliography and to Miss M VASSILAKI for counting the samples

J Inorg Nucl Chem 1963 Vol 25 pp 483 to 499 Pergamon Press Ltd Printed in Northern Ireland

RESIDUE ADSORPTION—I

SEPARATION OF STRONTIUM-90 AND YTTRIUM-90

H W KIRBY
Mound Laboratory,* Monsanto Research Corporation, Miamisburg, Ohio

(*Received* 20 *August* 1962)

Abstract—A new separation technique is presented, based on the tendency of the hydrolysed species of certain elements to become adsorbed on any available surface

To separate strontium-90 and yttrium-90, a dilute acid solution of the radioelements is evaporated to dryness, and the residue is covered with dilute ammonium hydroxide The solution is evaporated to dryness, and the residue is washed with distilled water Yttrium-90 remains adsorbed by the surface, while strontium-90 is separated in the distilled water

The adsorption of yttrium-90 is independent of the nature of the surface, being nearly quantitative on Teflon, glass, stainless steel, tantalum, gold and platinum The classical (Freundlich) isotherm is followed in the presence of yttrium carrier

The degree of separation (i e , the fraction of the strontium-90 remaining with the yttrium-90) is dependent upon the drying temperature and probably upon the nature of the surface

Yttrium-90 of any desired degree of purity can be prepared with negligible loss by repeated dissolution, hydrolysis and washing

The method is applicable to the determination of total rare earths in the picogram range

THIS paper presents a new separation technique based on the tendency of many elements to be adsorbed, under certain conditions, on any available surface such as the walls of a container

This phenomenon, sometimes erroneously called "radiocolloidal" adsorption is not limited to radioactive elements nor even to trace concentrations of hydrolysable species, although the high sensitivity of radiometric methods has greatly extended the lower limits at which adsorption studies can be carried out

For example, a common observation in precipitations from homogeneous phase is the strong tendency of slowly forming precipitates to be adsorbed by the walls of beakers.[1] It has, in fact, been suggested by H H WILLARD[2] that an appropriate goal would be to make this tendency quantitative, so that the mother liquor could be poured off without filtration and the precipitate weighed in the reaction vessel

In the method to be described, strontium-90 and yttrium-90 are deposited on a flat plate evaporated to dryness, and converted to hydroxides The hydroxides are evaporated to dryness and washed with water Yttrium-90 remains adsorbed nearly quantitatively, while strontium-90 is separated with the wash water The separation is independent of the nature of the surface

The separation of 28 year strontium-90 and its 64 hr daughter, yttrium-90, has been accomplished by carrier precipitation,(3) "radiocolloid" filtration,(4 5) electrolytic deposition,(6) liquid-liquid extraction,(7) anion exchange,(8) cation exchange,(9 10) and paper chromatography (11)

---

* Mound Laboratory is operated by Monsanto Research Corporation for the U S Atomic Energy Commission under Contract No AT-33-1-GEN-53

[1] GORDON, M L SALUTSKY and H H WILLARD, *Precipitation from Homogeneous Solution* p 11 Wiley, New York (1959)

[2] GORDON, Private communication (June, 1961)

[3] L SALUTSKY and H W KIRBY, *Analyt Chem* 27, 567 (1955)

In addition to these selected examples, numerous studies of the behaviour of the rare earth and alkaline earth elements offer the analyst a wide choice of methods from which separations appropriate to his specific needs can be adapted (12 13)

Thus, there is no scarcity of methods for the separation of strontium-90 and yttrium-90, and it is not the purpose of this paper merely to add to the list The strontium-90/yttrium-90 system was selected as a convenient vehicle for the investigation of some of the parameters of the method of residue absorption, which appears to be applicable to rare earth-alkaline earth separations in general and probably to other separations involving elements having significantly different hydrolytic tendencies

Preliminary observations

A solution of strontium-90/yttrium-90 had been obtained from Oak Ridge National Laboratory several years prior to the beginning of this work, and all of the solution had evaporated during the intervening years The bottle was leached with distilled water until further leaching recovered no additional radioactivity

A sample of the solution was β-counted The counting rate increased rapidly over a period of several days, indicating that the yttrium-90 had not been recovered from the original stock bottle

After a period of several months, the water solution of strontium-90 was again sampled and β-counted Although the yttrium-90 should have been in secular equilibrium by virtue of its short half-life, the β-counting rate of the sample increased for several days before atttaining a constant value, indicating that most of the newly formed yttrium-90 was being adsorbed on the sides of the storage vessel

Concentrated acid was added to make the solution approximately one normal in nitric acid The counting rate of the acidified solution immediately increased to twice its original value and remained stable thereafter

Concurrently, it was observed that, if a solution of protactinium-231 and its decay products (actinium-227, thorium-227, and radium-223) was evaporated to dryness on a flat plate, most of the radium-223 could be desorbed with distilled water, but dilute acid was required to remove actinium-227 Desorption of thorium-227 could usually be accomplished with hot 8N HNO_3, but the addition of a trace of hydrofluoric acid was sometimes necessary for quantitative removal. Recovery of protactinium from the residue required leaching with a mixture of nitric and hydrofluoric acids

---

(4) G K SCHWEITZER, B R STEIN and W M JACKSON, *J Amer Chem Soc* **75**, 793 (1953)

(5) J D KURBATOV, and M H KURBATOV, *J Phys Chem* **46**, 441 (1942)

(6) G LANGE, G HERRMANN and F STRASSMANN, *J Inorg Nucl Chem* **4**, 146 (1957)

(7) N P RUDENKO, *Zh Neorg Khim S S S R* **4**, 220 (1959)

(8) S MISUMI and T TAKETATSU, *J Inorg Nucl Chem* **20**, 127 (1961)

(9) E V MARATHE, *J Sci Industr Research (India)* **14 B**, 354 (1955)

(10) I J GAL and O S GAL, *Proceedings of the Second International Conference on Peaceful Uses of Atomic Energy, Geneva* **28**, 24 (1958)

(11) P C STEIN, *Analyt Chem* **34**, 348 (1962)

(12) D N SUNDERMAN and C W TOWNLEY, *The Radiochemistry of Barium, Calcium and Strontium* Natl Acad Sciences-Natl Research Council Report NAS-NS 3010 (1960)

(13) P C STEVENSON and W E NERVIK, *The Radiochemistry of the Rare Earths, Scandium, Yttrium and Actinium* Natl Acad Sciences-Natl Research Council Report NAS-NS 3020 (1961)

Further work with actinium-227, thorium-227, and radium-223 in the absence of protactinium-231 confirmed the quantitative differences in the adsorptive tendencies of the three radioelements and showed that lead-211 (a short-lived decay product of radium-223) was adsorbed as tenaciously as thorium-227

Neither the four-component protactinium chain, nor the three-component actinium chain, because of the complexity of their analytical problems, lend themselves well to a systematic investigation of the separation technique The strontium-90/yttrium-90 system, chemically analogous to radium-223/actinium-227 and barium-140/lanthanum-140, was therefore selected for this initial study of the method of separation by residue adsorption

Equipment and reagents

The strontium-90 solution described in the previous section was diluted with one normal nitric acid to provide a convenient counting rate A 250 μl sample of the diluted stock solution contained, by absolute beta counting, 0 867 μc of beta activity, or approximately three nanograms of strontium-90 and 0 8 pg of yttrium-90

β-bremsstrahlung counting of strontium-90 and yttrium-90 was done with a Nuclear Measurements Corporation PHA-ICA single channel scanning spectrometer equipped with a sodium iodide (thallium-activated) crystal, 2 in in diameter and ½ in thick The face of the crystal was covered with 0 001 in aluminium In this instrument, the gross β-bremsstrahlung counting-rate of the platinum-backed standard sample was 8 7 × 10^5 counts per min, uncorrected for coincidence Above 0 61 MeV, the gross counting-rate was 2 5 10^3 counts per min

Evaporations were carried out on a Precision hot plate equipped with a stepless bimetal thermoregulator Surface temperatures up to 200 C were determined, for each type of backing material, with Tempilstik or Tempilaq melting point compounds (Tempil Corporation, 132 West 22nd Street, New York 11, New York) Higher temperatures were supplied by a muffle furnace with a direct reading temperature indicator

Surface rugosity was measured with a mechanical profilometer (Micrometrical Mfg Co , Ann Arbor, Michigan) which reported the average depth of surface imperfections in microinches

All reagents, except yttrium carrier, were of analytical grade, and were used as received without further purification The yttrium oxide (99 ; % Y_2O_3) was prepared and analysed spectrographically by Y G Ishida of this Laboratory

Plastic retaining rings on glass and metal surfaces were prepared by spraying the surfaces, except for a circular masked area 15 mm in diameter, with Krylon Crystal Clear Spray Coating, a mixture of methyl and n-butyl methacrylate polymers dissolved in volatile aromatic hydrocarbons and propelled by fluorinated hydrocarbons (Krylon, Incorporated Norristown, Pennsylvania)

Transfer pipettes were made from commercial medicine droppers whose tips were drawn down to openings approximately 0 5 mm in diameter

Siliclad, a silicone coating (Clay-Adams, Incorporated, 141 East 25th Street, New York 10, New York) was used to coat the insides and tips of micropipets, eliminating the need for rinsing

EXPERIMENTAL

nple preparation and separation procedures

To provide uniform surface conditions, all experimental samples (except as noted in individual ses) were prepared identically Evaporations and other heating were at 90 C (3 C), except as noted The backing material was cleaned by agitating for 5 or 10 min in an alcoholic solution of potassium droxide The surface was rinsed thoroughly with distilled water and dried with absorbent paper

A methacrylate retaining ring was provided by masking the surface with an inverted glass vial, mm in diameter, and spraying the exposed area with Krylon coating The retaining ring was ted in the experiments with Teflon

The masking vial was removed, and the spray coating was allowed to dry thoroughly in air The ace was rinsed with distilled water, the excess water was shaken off, and the sample disk was dried he thermostatically controlled hot plate

The hot plate was adjusted with reference to the surface temperatures of glass, Teflon, or stainless steel, depending upon the material to be tested Stainless steel blanks (0 025 in thick) were used as temperature references for all metals and for Teflon film mounted on stainless steel backings The surface temperature was taken to be the average of the rated melting points of two Tempilstiks, one molten, the other solid at the stated temperature

The open (i e , uncoated) area of the sample disk was covered with 0 25 ml of 1N HNO_3 and heated for 5 min The acid was rinsed away with distilled water, the excess water was shaken off, and the disk was dried on the hot plate The open area was covered with 250 μl of the strontium-90/yttrium-90 stock solution, and the solution was evaporated to dryness The residue and the inner edge of the retaining ring were covered with 0 5 ml of recently boiled and cooled distilled water, and the solution was evaporated to dryness As the liquid evaporated, the aqueous solution contracted away from the retaining ring, and the evaporation was completed entirely within the open area Heating was continued for 5 min after the last visible trace of moisture had evaporated

The residue was covered with 0 25 ml of the selected reagent, and the solution was evaporated to dryness Heating was continued for 5 min after evaporation was completed

The gross counting rate of the sample above 0 61 MeV was determined during a standard 5 min counting and cooling period A standard sample of strontium-90/yttrium-90 in secular equilibrium and mounted on platinum, stainless steel or glass was counted just before or after the experimental sample to provide a basis for normalizing counting-rates obtained over a period of several days

Two types of separation procedure were used

(A) After being counted, the sample was washed for 60 sec in a stream of distilled water delivered by gravity from a storage bottle 6 ft overhead through an orifice 1 5 millimeters in diameter The total volume of water used to wash the sample was 560 ml

The wash water was discarded the excess water was shaken off, and the sample was dried at 90 C

(B) After being counted, the sample was returned to the hot plate, and the residue was covered with 0 5 ml of recently boiled and cooled distilled water The solution was heated for 5 min, and the remaining liquid (usually about 0 2 ml) was transferred by means of a transfer pipet to a second disk of the same material The residue was again covered with 0 5 ml of water, and the heating and transfer were repeated Both fractions were evaporated to dryness

Type A separations permitted rapid evaluation of many variables while minimizing potential manipulative errors Type B separations permitted the determination of material balances and multistage purifications of the separated radioisotopes

When the sample was dry, its β-bremsstrahlung counting rate above 0 61 MeV was determined Differential spectrometry was found to be unsatisfactory for routine use because of the inconvenience of preparing and maintaining standard samples of yttrium-90 having both adequate counting rates and high radio-chemical purity Instead, quantification of strontium-90 and yttrium-90 was accomplished routinely by the method of differential decay,(14) based on the yttrium-90 half-life of 64 029 hr(3) and the strontium-90 half-life of 28 years (15)

To simplify the differential decay calculations, the lower discriminator of the spectrometer was set on the 0 61 MeV γ-photopeak of bismuth-214 (radium C), and the upper discriminator was disabled Thus, only beta particles and bremsstrahlung due to yttrium-90 were counted (16)

The spectrum of an equilibrium mixture of strontium-90 and yttrium-90 is shown in Fig 1 Spectra of an equilibrium mixture and of the separated radioisotopes are shown in Fig 2 It is evident that 0 61 MeV is well beyond the maximum β-energy of strontium-90, as detected by the sodium iodide crystal The more probable maximum energy of the strontium-90 β-particles and bremsstrahlung is 0 54 MeV (16) This uncertainty does not, however, affect the reliability of the differential decay calculations, and the use of the higher energy limit insures that no strontium-90 activity will be counted directly

Nature of the adsorbent surface

The materials listed in Table 1 were tested to determine the effect of the nature of the substrate on the degree of separation All of the surfaces were prepared as described above, except that the Teflon

---

(14) H W KIRBY, *Analyt Chem* **26**, 1063 (1954)

(15) W H SULLIVAN, *Trilinear Chart of Nuclides*, U S A E C , January (1957)

(16) D STROMINGER, J M HOLLANDER and G T SEABORG, *Revs Mod Phys* **30**, 585 (1958)

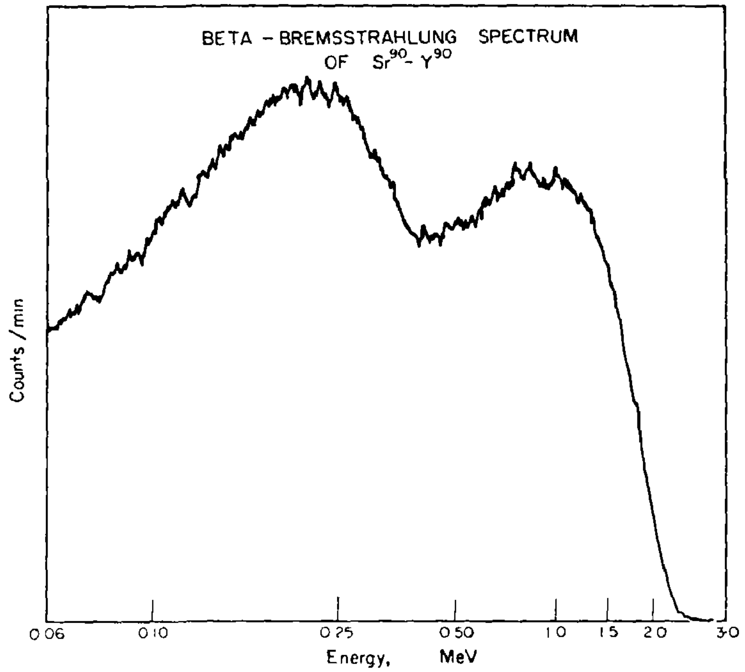

BETA - BREMSSTRAHLUNG SPECTRUM
OF Sr90- Y90
Counts / min
0 06
0 10
0 25
0 50
1 0
1 5
2 0
3 0
Energy, MeV

FIG 1

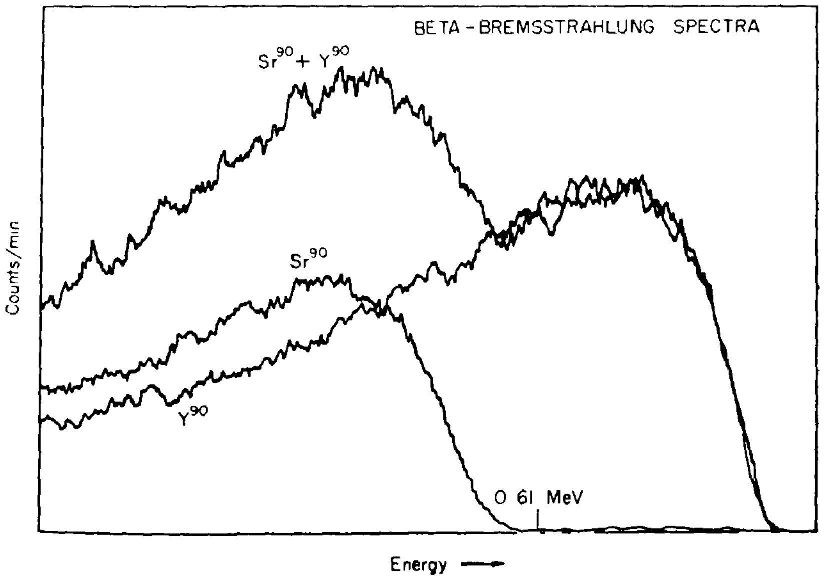

BETA - BREMSSTRAHLUNG SPECTRA
Sr90+ Y90
Sr90
Y90
0 61 MeV
Counts/min
Energy →

FIG 2

TABLE I ADSORPTION OF STRONTIUM-90 AND YTTRIUM-90 HYDROXIDES
Effect of Substrate Material
(Maximum Temperature 90 C)

Number	Substrate	Sepn type	% Retained ^{90}Sr	^{90}Y	Separation* factor
281-G	Soda-lime glass	A	18 1	95 3	5 3
241	Soda-lime glass	B	9 7	98 7	10 2
281-H	Borosilicate glass (Pyrex)	A	19 0	96 4	5 1
269	Borosilicate glass (Pyrex)	B	18 5	94 1	5 1
252	Polytetrafluoroethylene (Teflon)	B	23 8	96 4	4 1
281-I	Teflon film on stainless	A	1 7	63 9	37 6
255	Teflon film on stainless	B	10 7	74 6	7 0
256	Teflon film on stainless	B	4 1	94 2	23 0
281-A	Stainless steel	A	7 9	96 4	12 2
239	Stainless steel	B	27 7	98 2	3 5
259	Stainless steel	B	11 9	99 2	8 3
281-I	Gold	A	3 6	94 2	26 2
281-D	Gold-plated stainless	A	2 9	83 3	28 7
240	Gold-plated stainless	B	2 1	99 1	47 2
294-B	Gold-plated stainless	B	4 0	99 9	25 0
281-B	Tantalum (Annealed, dull)	A	10 5	95 9	9 1
258	Tantalum (Annealed, dull)	B	27 6	99 2	3 6
281-C	Tantalum (Unannealed, bright)	A	12 9	95 7	7 4
250-B	Platinum	A	14 0	98 5	7 0
251	Platinum	B	9 2	96 8	10 5

* Separation factor = $\%^{90}$Y/$\%^{90}$Sr

film cemented to a stainless steel backing was cleaned with ethyl alcohol instead of alcoholic potassium hydroxide In each case, the ' selected reagent" consisted of 0 2 ml of previously boiled and cooled distilled water and one drop (0 05 ml) of concentrated ammonium hydroxide (This mixture is referred to hereafter as 2M NH_4OH)

No significant differences were observed in the results obtained by the two separation methods Except for two Teflon surfaces and one gold surface, over 90 per cent of the yttrium-90 was retained regardless of the nature of the surface material or of the type of separation

All surfaces adsorbed significantly less strontium-90 than yttrium-90 Although the degree of separation varied widely even among similar surfaces, the percentage of yttrium-90 retained by the washed surface was at least 3 5 times as great as the percentage of strontium-90

Effect of temperature and desiccation

The same procedures were used to study the effect on lime glass, stainless steel, gold and platinum of exposure to various temperatures For experiments at 90 C or above, samples were counted before the addition of 2M NH_4OH to the dried residue

After the ammonium hydroxide solution had evaporated to dryness, the sample was heated for an additional five minutes at 90°C, then transferred to a second hot plate or to a muffle furnace previously set at a higher temperature After 5 min at the elevated temperature, the sample was returned to the 90° hot plate for 5 min of temperature equilibration before type B separations were carried out For type A separations, samples were cooled to room temperature for at least five minutes before being washed

Four separations of type A were carried out on platinum at temperatures below 90°C Modifications were made in the standard waiting periods between reagent additions to compensate for the slower evaporation rates Since evaporation of 0 5 ml of water at 55°C required 65 min (vs 12 min at 90°C), heating was continued for 30 min instead of the usual five Evaporations at room temperature

(27–28 C) were usually carried out overnight since 0 5 ml of H_2O required 4½ hr for complete evaporation Drying of two of the three room temperature samples was completed in an evacuated bell jar in the presence of anhydrous magnesium perchlorate

All materials tested retained yttrium-90 essentially quantitatively at 90 C and above The adsorption of strontium-90 increased with increasing temperature, but the temperature at which this increase became significant was different for different materials

TABLE 2 —ADSORPTION OF STRONTIUM-90 AND YTTRIUM-90 HYDROXIDES ON PLATINUM

EFFECT OF TEMPERATURE

Number	Separation type	Maximum temperature (C)	% Retained	
			^{90}Sr	^{90}Y
297-A	A	28	2 6	69 0
298-A*	A	28	2 0	71 9
298-B†	A	28	3 3	81 0
297-B	A	55	8 8	90 7
250-B	A	90	14 0	98 5
251	B	90	9 2	96 8
280-19	A	200	8 2	99 7
253-1	B	300	12 6	99 9
253-3‡	B	400	50 0	99 8
280-17	A	500	64 1	95 1
253-2‡	B	500	75 7	100 3
280-18	A	1000	79 7	98 4

* Vacuum desiccated 1 hr

† Vacuum desiccated 19 hr

‡ Plastic retaining ring burned off and surface became very hydrophilic Washing was carried out with two 0 25 ml portions of H_2O instead of standard 0 5 ml portions

Lime glass and stainless steel showed increased retention of strontium-90 at 150 C, but the retention of strontium-90 by gold and platinum did not increase significantly between 90 and 300 C

The results for platinum over the range 28 to 1000 C are given in Table 2 Evaporation at room temperature resulted in lower retention of yttrium-90, but the retention was significantly enhanced by vacuum desiccation The highest separation factor achieved (relative retention of yttrium-90 and strontium-90) was 36 3 for a sample which was vacuum desiccated for 1 hr at room temperature, but the yttrium-90 yield was only 71 9 per cent A yield of 81 0 per cent and a separation factor of 24 9 was found for a sample which was vacuum desiccated at room temperature for 19 hr

Effect of the residual anion

Seven volatile and five non-volatile reagents (Tables 3 and 4, respectively) were studied with platinum at a maximum temperature of 90 C Separation type A was used throughout

The total amounts of strontium-90 and yttrium-90 in the carrier-free residue were approximately 3×10^{-8} and 1×10^{-11} mmole, respectively Nevertheless, the concentration of the added reagent is significant, even for the volatile reagents Furthermore, when the residue from an acid reagent was covered with distilled water and re-evaporated, the retention of yttrium-90 was enhanced, suggesting that residual acid had been redissolved and volatilized

There was no consistency among the several reagents in the relationship between concentration and per cent adsorption With hydrofluoric acid, an increase in concentration resulted in increased adsorption of both strontium-90 and yttrium-90, but the reverse was true for hydrochloric, nitric and acetic acids

The results with NH_4HCO_3, which decomposes at about 60 C to yield NH_3 and CO_2, were the

TABLE 3 ADSORPTION OF STRONTIUM-90 AND YTTRIUM-90 ON PLATINUM AT 90 C

EFFECT OF VOLATILE REAGENTS

Number	Reagent	% Retained		Separation factor
		^{90}Sr	^{90}Y	
250-A	H_2O	1 6	57 0	35 6
283-20*	(1 M HNO_3) + 2H_2O	0 5	44 5	89 0
275-6*	(6 M HCl) + 2H_2O	2 3	14 7	6 4
303-23	0 01 M NH_4OH	10 5	87 3	8 3
303-24	0 1 M NH_4OH	13 0	96 1	7 4
250-B	2 M NH_4OH	14 0	98 5	7 0
293-27	0 001 M NH_4HCO_3	1 4	63 3	45 2
293-26	0 1 M NH_4HCO_3	9 9	89 3	9 0
250-D	0 01 M HI	7 4	29 3	4 0
277-11	0 1 M HI	14 4	71 6	5 0
278-15	1 M HF	19 6	64 9	3 3
277-9	0 02 M HNO_3	1 0	25 6	25 6
257-D	1 M HNO_3	0 7	15 1	21 6
278-13	0 01 M HCl	2 0	10 8	5 4
257-C	1 M HCl	4 5	4 2	0 9
274-3	6 M HCl	3 4	7 0	2 1
302-9	0 1 M CH_3COOH	8 2	52 8	6 5
278-14	0 15 M CH_3COOH	15 7	29 2	1 9
257-F	1 5 M CH_3COOH	0 7	8 6	12 3

* After evaporation to dryness, the acid residue was covered with 0 5 ml H_2O and dried, covered again with 0 5 ml H_2O, dried and washed

TABLE 4 ADSORPTION OF STRONTIUM-90 AND YTTRIUM-90 ON PLATINUM AT 90 C

EFFECT OF NON-VOLATILE REAGENTS

Number	Reagent	% Retained		Separation factor
		^{90}Sr	^{90}Y	
250-E	0 001 M $NH_4H_2PO_4$	19 2	60 7	3 2
277-12	0 01 M $NH_4H_2PO_4$	6 8	68 5	10 1
304-25*	(0 1 M $NH_4H_2PO_4$) + 2H_2O	0 2	4 7	22 0
283-30	0 01 M NaOH	4 7	50 4	10 7
283-29	0 1 M NaOH	1 4	49 0	35 0
293-28	1 M NaOH	0 8	0 7	0 9
250-C	0 001 M $(COOH)_2$	27 8	46 2	1 7
277-10	0 01 M $(COOH)_2$	1 2	12 4	10 3
250-F	0 001 M $(NH_4)_2SO_4$	1 5	22 0	14 7
278-16	0 01 M $(NH_4)_2SO_4$	0 4	4 8	3 2
283-22	0 000001 M Na_2EDTA	10 0	51 8	5 2
283-23	0 00001 M Na_2EDTA	12 3	45 9	3 7
285-1	0 00002 M Na_2EDTA	1 8	34 4	19 1
285-25	0 00005 M Na_2EDTA	4 5	4 5	1 0
283-24	0 0001 M Na_2EDTA	2 2	1 2	0 5

* After evaporation to dryness, the phosphate residue was covered with 0 5 ml H_2O and dried, covered again with 0 5 ml H_2O, dried and washed

only ones comparable in yttrium-90 yield to those with NH_4OH The presence of carbonate ion did not significantly change the degree of strontium-90 retention Because of the vigorous evolution of CO_2 and the consequent danger of spattering, it was not feasible to test NH_4HCO_3 at concentrations above 0 1 molar

Separations factors less than unity were obtained at some HCl concentrations, but were not reproducible In all such cases, yields of strontium-90 and yttrium-90 were below 10 per cent, and the low ratios were probably fortuitous

Increasing concentrations of non-volatile reagents in general gave lower yields of yttrium-90 With the disodium salt of ethylene diamine tetra-acetic acid (Na_2EDTA), desorption of yttrium-90 was nearly quantitative when the total amount of Na_2EDTA was approximately $1\ 25 \times 10^{-2}$ millimole

Except with ammonium dihydrogen phosphate, the highest yttrium-90 yield achieved with non-volatile reagents was lower than that with distilled water

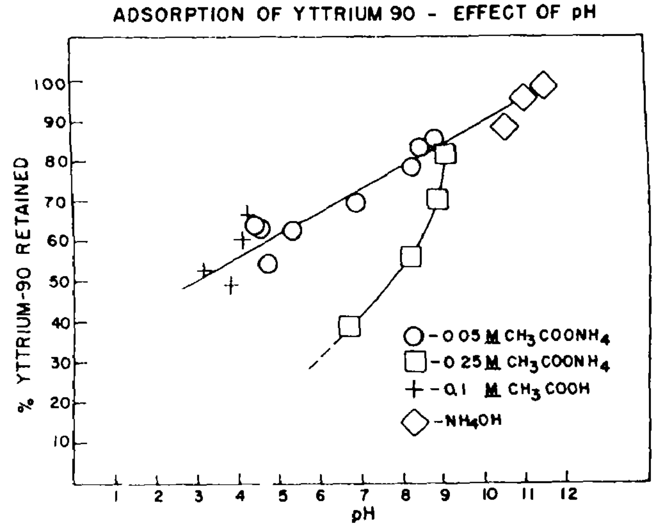


FIG 3

Effect of pH

Standardized ammonium hydroxide and acetic acid were mixed in various proportions to provide 0 05 and 0 25 molar ammonium acetate containing excess acid or base and 0 1 molar acetic acid containing various concentrations of ammonium acetate Procedure A was followed throughout

Fig 3 shows the percentage of yttrium-90 adsorbed on platinum at 90 C as a function of the initial pH Results for three concentrations of ammonium hydroxide are included for comparison

In general increasing the initial pH resulted in higher retention of yttrium-90, but an increase in salt concentration at a given pH inhibited the adsorption Strontium-90 retention (not shown) was increased, for reagents containing ammonium acetate, from 0 2 per cent at pH 6 7 to 6 3 per cent at pH 9 1 with separation factors of 207 and 13, respectively In pure ammonium hydroxide, the strontium-90 retention increased from 10 5 to 14 0 per cent with increasing pH

Effect of carrier additions

Strontium-90/yttrium-90 aliquots were mounted on platinum and evaporated to dryness Strontium and/or yttrium nitrate carrier in 1 M HNO_3 was added, and the solution was again evaporated to dryness The residue was covered with 0 5 ml of water, and Procedure A was followed, with 2 M NH_4OH as the selected reagent

A logarithmic plot of the amount of yttrium adsorbed versus the amount added (Fig 4) yielded an adsorption isotherm which was linear with up to 25 μg of added yttrium The maximum retention of yttrium was approximately 12 μg with 25, 50 and 100 μg added However, yttrium retention dropped sharply when larger amounts were added Only 1 6 μg of yttrium was retained when one milligram of yttrium was added

Addition of strontium carrier alone or in combination with yttrium carrier had, in general, an inhibiting effect on the retention of yttrium However, the effect of strontium addition on strontium retention was ambiguous and, within experimental limits, appeared to be random (Table 5)

The addition of strontium had approximately the same effect as the addition of sodium (Cf Table 4)

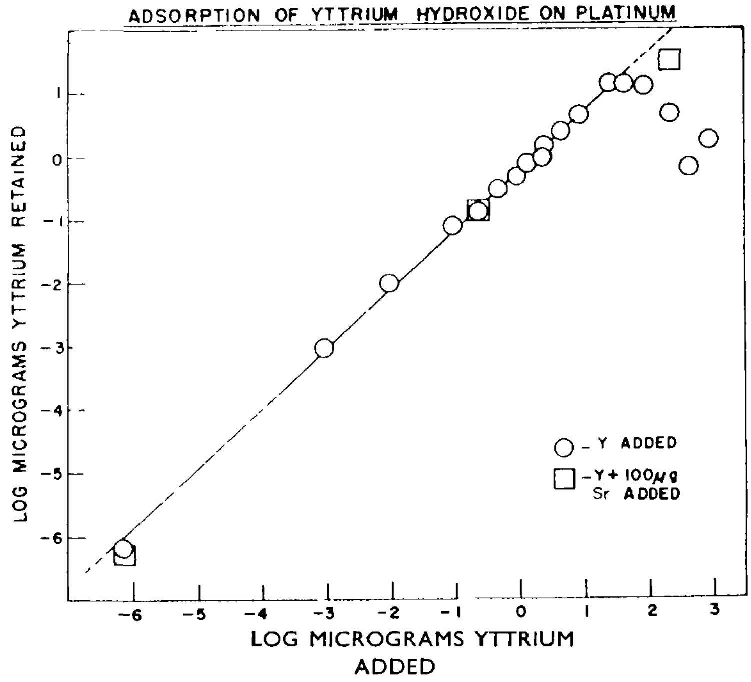


FIG 4

Surface rugosity and area

With carrier-free strontium-90/yttrium-90, there was a significant difference between the adsorptivity of mill-finished or mechanically buffed bright platinum and platinum which had been hand-polished with abrasives to a dull finish The dull surface retained more yttrium-90 than did the bright surface, when the same reagent was tested on both by procedure A (Table 6)

However, when 100 μg of yttrium was added to the carrier-free samples, approximately the same amount of yttrium was retained by both the bright and the dull platinum surfaces Similar tests on other surfaces indicated that the apparent surface area was more significant than the rugosity in determining the amount of yttrium that could be adsorbed (Table 7)

Beaker and crucible separations

A sample of ^{90}Sr/Y^{90} was evaporated to dryness in a one-milliliter Pyrex beaker, and 0 25 ml of 2 M NH_4OH was added The solution was evaporated to dryness, and 0 25 milliliter of 10 ^{4} N HNO_3 was added This solution was evaporated to dryness The beaker was leached three times with 0 25 ml milliliter portions of previously boiled and cooled distilled water, heated for 2 min before each transfer All three leach solutions were deposited on a single stainless steel disk and evaporated to dryness

The beaker was leached twice with 0 25 ml portions of hot 1 M HNO_3, and the solutions were transferred to a second stainless steel disk The distribution of ^{90}Sr and ^{90}Y was as follows

	^{90}Sr (%)	^{90}Y (%)
Leached with H_2O	48 8	4 1
Leached with 1 N HNO_3	53 7	96 3
Totals	102 5	100 4

TABLE 5.—ADSORPTION OF STRONTIUM AND YTTRIUM HYDROXIDES ON BRIGHT PLATINUM AT 90° C

EFFECT OF CARRIER ADDITIONS

Number	Carrier added (μg) Sr	Y	Retained Sr(%)	Sr(μg)	Y(%)	Y(μg)	Separation factor
299-1		1000	0.02		0.16	1.6	6.9
299-2		500	0.12		0.13	0.6	1.1
299-3		250	0.33		1.7	4.2	5.0
301-35	100	250	0.49	0.49	10.5	26.3	21.6
299-4		100	1.5		11.5	11.5	7.4
299-5		50	2.0		23.5	11.8	11.7
299-6		25	5.5		49.1	12.3	9.0
299-7		10	3.5		41.0	4.1	11.9
299-8		5	5.0		45.5	2.3	9.2
299-9		2.5	9.0		35.3	0.9	3.9
299-31		2.5	11.9		45.7	1.1	3.9
301-2	100	2.5	15.7	15.7	32.2	0.8	2.1
299-30		1.5	7.9		47.9	0.7	6.1
299-10		1.0	10.8		43.4	0.4	4.0
299-29		0.5	8.8		47.7	0.3	6.6
299-32		0.25	16.3		46.4	0.1	2.8
301-3	100	0.25	5.8	5.8	50.8	0.1	8.8
299-26		0.1	4.4		75.3	0.08	17.3
299-27		0.01	5.5		93.4	0.009	17.0
299-28		0.001	5.2		94.0	0.0009	18.2
301-34	1000		0.2	1.8	32.3		180
301-33	250		1.2	3.0	68.6		57.8
301-1	100		3.3	3.3	65.9		20.0
301-32	50		10.2	5.1	83.9		8.2
301-4	10		16.0	1.6	81.2		5.1
301-5	1		1.3	0.01	84.8		66.5
301-6	0.1		3.0	0.003	87.1		29.5
301-7	0.01		2.5	0.0003	84.1		33.1
301-8			4.6		91.6		19.8

TABLE 6.—ADSORPTION OF STRONTIUM-90 AND YTTRIUM-90 ON PLATINUM AT 90° C

EFFECT OF SURFACE FINISH

Number	Finish	Reagent	% Retained ^{90}Sr	^{90}Y
250-A	Bright	H_2O	1.6	57.0
292-21	Dull	H_2O	7.9	84.5
293-27	Bright	0.001 M NH_4HCO_3	1.4	63.3
292-2	Dull	0.001 M NH_4HCO_3	12.3	85.8
293-26	Bright	0.1 M NH_4HCO_3	9.9	89.3
292-1	Dull	0.1 M NH_4HCO_3	9.9	93.2

TABLE 7 — YTTRIUM RETAINED BY VARIOUS SURFACES
(Yttrium added 100 μg, Reagent 2 M NH_4OH)

Number	Surface	Apparent area (cm²)	Y Retained (μg/cm²)	Relative retention	Relative rugosity
300-A	Soda-lime glass	1 8	6 4	1 0	1 0
299-4	Bright platinum	1 8	6 5	1 0	2 9
306-4R	Dull platinum	1 8	6 9	1 1	5 0
300-B	Teflon film	0 4	9 3	1 5	2 9
300-C	Stainless steel	1 8	11 6	1 8	1 2
300-D	Stainless steel	4 9	11 4	1 8	1 2

Similar results were obtained when the separation was repeated in 5 ml Pyrex beakers, including one which was coated internally with Siliclad Experimentation indicated that the loss of strontium-90 resulted from the thermal gradient between the top and the bottom of the beaker

To test this conclusion separations were carried out in a soft glass vial (coated internally with Siliclad), a stainless steel crucible, and a platinum crucible All three vessels were placed in a drilled aluminium block which was set on the hot plate The temperature was measured with Tempilaq in a glass vial heated in the same block

Aliquots of the strontium-90/yttrium-90 solution were transferred to the three jacketed vessels and evaporated to dryness at 90 C One-half millilitre of previously boiled and cooled distilled water and one drop of concentrated ammonium hydroxide was added to each dry vessel, and the solutions were evaporated to dryness One-half millilitre of 10^{-4} N HNO_3 was added to each dry vessel, and the solutions were evaporated overnight at 90 C Each vessel was leached with two 0 5 ml portions of previously boiled and cooled distilled water, which were heated for five minutes at 90° before being transferred to stainless steel disks The vessels were then washed with two 0 5 ml portions of 0 01 M HNO_3, also heated for 5 min before transfer to second stainless steel disks The results showed separations comparable to those obtained on flat disks (Table 8)

TABLE 8 — SEPARATION OF STRONTIUM-90 AND YTTRIUM-90 HYDROXIDES IN JACKETED GLASS, STAINLESS STEEL, AND PLATINUM VESSELS

Number	Vessel	Leached with H_2O		Leached with 0 01 M HNO_3	
		^{90}Sr(%)	^{90}Y(%)	^{90}Sr(%)	^{90}Y(%)
272-1	Glass vial	82 5	3 2	16 0	91 1
272-2	Stainless crucible	90 8	7 7	4 1	96 1
272-3	Platinum crucible	88 5	7 9	7 1	88 1

Cleaning and masking

The cleaning and masking steps used in the experimental procedures were adopted to provide uniformity of experimental conditions It was of interest to determine the extent to which these steps contributed to the results obtained

A stainless steel disk was cleaned with acetone and benzene until no grease or gum was visible The customary cleaning with alcoholic KOH, the plastic retaining ring, and the preliminary treatment with hot 1 M HNO_3 were omitted

A 250 μl aliquot of Sr^{90}/Y^{90} in 1 M HNO_3 covered an area approximately 25 millimeters in diameter instead of the usual 15 mm defined by the retaining ring When the hydroxide treatment was completed and the residue leached with distilled water by separation procedure B, it was possible to heat for only 2 min instead of the usual five because of the relatively rapid evaporation from the larger surface area

Nevertheless, the residue retained 96 3 per cent of the yttrium-90 and 14 3 per cent of the strontium-90 indicating that neither the cleaning solutions nor the methacrylate ring were necessary for the separation except for their intended purposes

Purification of strontium-90 and yttrium-90

Although the hydroxide residues were washed with 560 ml of water in procedure A and with 1 ml in procedure B, the results were comparable No further improvement in purity could be expected from additional washing with water However, both fractions could be purified by redissolution in nitric acid followed by hydroxide metathesis and water leaching

A platinum-clad stainless steel disk was cleaned with distilled water and acetone, then masked and sprayed with methacrylate as usual The strontium-90/yttrium-90 mixture in 1 M HNO_3 was transferred to the disk, evaporated to dryness, covered with 2 M NH_4OH, and dried at 90 C The residue was leached with three 0 25 ml portions of hot distilled water, the leachings being transferred to a second disk

The residue on the first disk was covered with 0 25 ml of 0 1 M HNO_3, evaporated to dryness, covered with 2 M NH_4OH, dried and leached as before The leachings were transferred to a third disk

The redissolution, hydroxide treatment and leaching with water were repeated, and the leachings transferred to a fourth disk

Finally, the residue was redissolved, treated with hydroxide, dried and leached with three 0 25 ml portions of 10^{-3} M HNO_3, the leachings being transferred to a fifth disk

The results below were computed by differential spectrometry, based on the assumption that the original residue of yttrium-90 was free of strontium-90 after four successive separations

Fraction	$^{90}Sr(\%)$	$^{90}Y(\%)$
First H_2O	96 7	0 9
Second H_2O	5 0	1 3
Third H_2O	0 4	1 6
10^{-3} M HNO_3	0 15	4 6
Original disk (residual)	0 0*	90 6
Totals	102 2	98 9

* Assumed

Purification of the strontium-90 fraction can be accomplished in a similar manner The strontium-90 is readily transferred from one disk to the next leaving behind 90 per cent or more of any yttrium-90 previously transferred or produced by decay However since yttrium-90 grows initially at the rate of approximately 0 1 per cent in 5 min decontamination of the strontium-90 much below that order of magnitude is impractical

Metathesis of chloride residues

Of the reagents listed in Table 3, the most effective in inhibiting the adsorption of yttrium-90 was hydrochloric acid at all concentrations To test the permanence of this effect an aliquot of the strontium-90/yttrium-90 stock solution was evaporated to dryness on a platinum disk and the residue covered with 6 M HCl The solution was evaporated to dryness and the residue covered with 2 M NH_4OH The solution was evaporated to dryness, and the residue was leached twice with 0 5 ml of previously boiled and cooled distilled water as in procedure B

The strontium-90 fraction contained 2 1 per cent of the yttrium-90 and the yttrium-90 fraction retained 3 9 per cent of the strontium-90

Autoradiography

An aliquot of the strontium-90/yttrium-90 stock solution was mounted on each of two gold-clad stainless steel disks

Both samples were carried through the standard procedure with 2 M NH_4OH, except that only one of the samples was leached with water by procedure B The other sample was retained as a standard

The three disks were autoradiographed on Ilford X-ray film (Fig 5), and their beta-bremsstrahlung spectra were recorded (Fig 2)

There was a distinct difference in the distribution of the yttrium-90 and strontium-90 hydroxides Whereas the unseparated mixture covered the entire open area (15 mm in diameter) of the gold surface, the strontium-90 concentrated at the edge of the plastic in a ring 3 mm thick, while the yttrium-90 covered an area approximately 10 mm in diameter in the center of the gold surface

DISCUSSION AND CONCLUSIONS

It seems evident from the foregoing experimental results that the separation of yttrium-90 and strontium-90 hydroxides is based on qualitative differences in chemical behaviour rather than on quantitative or kinetic differences

The nearly identical adsorption of yttrium-90 hydroxide by substrates of widely differing chemical compositions (Table 1) is characteristic of physisorption, which is always non-specific(17)

Strontium-90 adsorption, on the other hand, ranged from an average of 2 9 per cent on gold to 18 8 per cent on Pyrex Although the strontium-90 results were erratic (extremes of 1 7 and 23 8 per cent on Teflon), they indicate that the nature of the substrate is significant and, hence, that the mechanism of strontium-90 adsorption probably differs from that of yttrium-90 in kind as well as magnitude

The same conclusion can be derived from the results obtained at different temperatures (Table 2) Yttrium-90 adsorption was nearly independent of temperature over the range 28°C–1000°C The low value (69 0 per cent) found at 28°C can be attributed to the presence of a film of adsorbed moisture, as shown by the substantial increase in adsorption under the influence of prolonged vacuum desiccation Strontium-90 adsorption was a function of both substrate and temperature, again indicating chemisorption

Nearly all precious metal surfaces were readily decontaminated with hot 6 N HCl after the methacrylate ring had been removed with acetone However, for complete removal of beta activity from surfaces which had been heated above 90 C, brief exposure to aqua regia was necessary One platinum disk which had been heated to 1000°C retained 0 6 per cent of the original activity (subsequently identified as strontium-90) even after the surface was deeply etched with aqua regia This observation supports the conclusion that strontium-90 retention is due to the formation of a surface chemical compound or solid solution

Finally, autoradiography showed striking differences in the drying patterns of the two radioelements (Fig 5) The estimated area covered by the yttrium-90 was only about twice as great as that covered by the strontium-90, yet the per cent retention by the gold surface was twenty-five times as high for yttrium-90 as for strontium-90

There is, apparently, no synergic effect and, from the standpoint of yttrium-90 yield, the presence of strontium-90 is almost irrelevant The addition of relatively massive amounts of strontium carrier had some effect on the degree of adsorption of yttrium-90 (Table 5), but this can be ascribed to the fact that the dried strontium hydroxide acted as a water-soluble substrate for deposition and subsequent desorption of yttrium-90

(17) S J GREGG, *The Surface Chemistry of Solids* Reinhold, New York (1961)

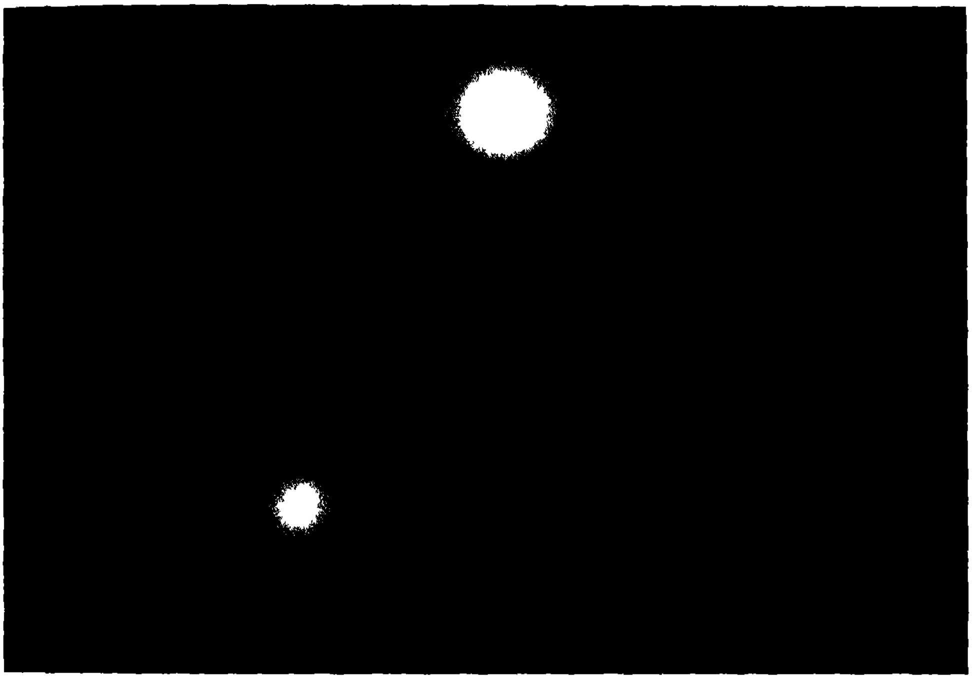


FIG. 5. Autoradiographs of ^{90}Sr-^{90}Y (upper), ^{90}Y (left) and ^{90}Sr (right).

The data on the effect of residual anions (Tables 3 and 4) are somewhat more equivocal, particularly with regard to the non-volatile reagents, where the presence of a water-soluble residue with a relatively high specific surface would inhibit retention by the permanent substrate

In general, however, the data suggest that yttrium-90 is not adsorbed as a simple cation but as a molecule or coordination compound, and both the nature and concentration of the residual anion exert a significant influence

BELLONI *et al*,(18) working with lanthanides under equilibrium conditions, have assumed that adsorption of cations is due to the electrostatic attraction of a primary layer of adsorbed anions, and that the effect of pH is explained by competitive adsorption of H^+ ions While the present work is not strictly comparable because of the nonequilibrium conditions, there seems no reason to prefer a second-order ionic mechanism to a first order adsorption of undissociated molecules

The degree of adsorption of yttrium-90 is at least a qualitative function of the solubility of the yttrium salt Those reagents which are commonly used in the precipitation and gravimetric determination of yttrium also significantly enhance the retention of yttrium-90 platinum

Quantitative data relating to the solubilities of yttrium fluoride, carbonate, and phosphate are unavailable, but the solubility product of yttrium oxalate is reported as 5 34 $\times$ 10^{-29} (19) and that of yttrium hydroxide as 5 2 $\times$ 10^{-22} (20) Since the adsorption of these compounds is in reverse order, the hydroxide retention being approximately twice that of the oxalate, there is evidently no simple relationship between the solubility of macroscopic amounts of yttrium salts and their adsorption More probably, the role of the precipitant lies in producing a molecular aggregate of suitable crystal structure, dimensions and charge

The difference between the effects of nitric and hydrochloric acids is striking (Table 3) Both yttrium nitrate and yttrium chloride are highly soluble compounds, yet the adsorption of yttrium-90 from a nitrate residue was significantly higher than that from a chloride residue This difference was magnified by repeated redissolution and evaporation with water

Adsorption is an exothermic process,(17) and it is possible that partial pyrolysis of the $Y(NO_3)_3\ 6H_2O$, even at the moderate temperature of 90°C, results in the formation of basic yttrium nitrate, $Y(NO_3)_3\ Y(OH)_3\ 3H_2O$ (21)

Under equilibrium conditions, adsorption increases with pH, reaching a maximum at a pH value, usually between three and six, which is characteristic of the radio element (22 23) No such maximum was found in the present work, instead, as in ultrafiltration, the adsorption of yttrium-90 continued to increase with pH until nearly quantitative adsorption was attained (Fig 3)

The pH results are particularly interesting with regard to the difference in the adsorption from 0 05 and 0 25 molar ammonium acetate The rapid convergence of the two pH curves suggests that yttrium hydroxide forms instantaneously to the

---

I BELLONI, M HAÏSSINSKY and H N SALAMA, *J Phys Chem* **63,** 881 (1959)

A M FEIBUSH, K ROWLEY and L GORDON, *Analyt Chem* **30,** 1610 (1958)

T MOELLER and H E KREMERS, *Chem Rev* **37,** 97 (1945)

R C VICKERY, *Chemistry of the Lanthanons*, p 279 Academic Press, New York (1953)

I E STARIK, *Khim Nauk Prom* S S S R **4,** 448 (1959)

I BELLONI-COFLER, Doctoral Thesis, Faculté des Sciences de l'Université de Paris (1961) extent of the free hydroxyl ion available in the original solution, and is redissolved only slowly by the free acetic acid resulting from the thermal decomposition of ammonium acetate. This behaviour tends to confirm the assumption that yttrium-90 is adsorbed as a molecule rather than as a cation attracted electrostatically to a primary layer of adsorbed anions.

The adsorption of yttrium hydroxide as a function of the yttrium concentration obeys the Freundlich isotherm over a wide range, from 8×10^{-7} μg (carrier-free ^{90}Y) to 25 μg of total yttrium (Fig. 4). The slight deviation from linearity at the carrier-free end of the isotherm is probably attributable to the presence of an indeterminate amount of zirconium-90, the stable end product of strontium-90/yttrium-90 decay.

The crystalline arrangement of yttrium hydroxide is such that each yttrium atom is surrounded by nine hydroxyl groups, whose nearest approach to each other is 2.78 Å.[24] If it is assumed that each yttrium atom occupies the peak of a pyramid whose base consists of three hydroxyl groups, the maximum amount of yttrium which can be held in a monolayer on a surface area of 1.75 cm^2 is 0.8 μg. This is the same order of magnitude as the yttrium retained with 0.5 and 1.0 mg of total yttrium (Table 5).

The maximum amount of adsorbed yttrium found experimentally was 12.3 μg, or approximately fifteen times as great as that of the hypothetical monolayer. The adsorptive process cannot, however, be considered merely the stacking of fifteen monolayers held by progressively weaker van der Waals forces. This would require that the amount of adsorbed yttrium reach a maximum value and remain at that level despite any further increase in yttrium concentration. As seen in Fig. 4, yttrium adsorption, while tending to reach a constant saturation level, dropped sharply when the total yttrium exceeded 100 μg.

Decontamination of yttrium-91 deposited on painted surfaces was found by CHANDLER and SHELBERG[25] to be a function of micelle concentration. For each of two soap solutions decontamination began at or near the critical micelle concentration[26] and increased rapidly with micellar concentration up to two or three times the critical value. Decontamination was independent of surface tension. The authors suggested that decontamination resulted from competition between the micellar interface and the original surface.

By analogy with the concept of the critical micelle concentration, the sharp decrease in the amount of yttrium adsorption may reflect the existence of a critical precipitate concentration, in this case 0.004 M yttrium (100 μg in 0.25 ml of 2 M NH_4OH), at which point the intermolecular forces of the yttrium hydroxide aggregate would counterbalance the weakly polar forces tending to bond all but the first monolayer to the substrate.

This interpretation is supported by the results in Tables 6 and 7. Surface rugosity was a significant factor in the adsorption of carrier-free yttrium-90, but at the 100 μg level there was no correlation between rugosity and adsorption, suggesting that the micelles were too large to be affected by the increase in real surface due to microscopic imperfections in the substrate.

---

[24] R. W. G. WYCKOFF, *Crystal Structures*, Vol. 2, Chap. 5, p. 25a (supplement). Interscience, New York (1957).

[25] R. C. CHANDLER and W. E. SHELBERG, *J. Colloid Science* **10**, 393 (1955).

[26] J. W. McBAIN, *Colloid Science*, p. 251. Heath (1950).

Thus, desorption of yttrium hydroxide, or its failure to be adsorbed at levels greater than the critical concentration, does not imply solubilization but the reverse, namely, incipient precipitation

The linear portion of the adsorption isotherm has an interesting analytical application KURBATOV and KURBATOV[27], in a study of the adsorption of barium by ferric hydroxide, proposed the use of adsorption isotherms for the determination of stable elements at very low concentrations A similar technique, using residue adsorption instead of filtration, can evidently be applied to concentrations of yttrium in the picogram and nanogram range

A considerable mystique has grown up around "radiocolloids" since their discovery by PANETH in 1912, and it has become routine to take precautions against the loss of radioactivity by adsorption on the walls of containers

For example, standard solutions of strontium-90/yttrium-90 are prepared by the U S National Bureau of Standards with strontium and yttrium added (9 μg/ml of each) 'to insure that the ^{90}Y activity remains in equilibrium and is not lost to the glassware by adsorption" [28] Since the solutions are one normal in hydrochloric acid, it seems unlikely from the present work that such adsorption would occur, or that the small amount of added carrier would serve a useful purpose

The term, "radiocolloid", is itself a misnomer, implying that colloid formation at very low concentrations is a unique property of radioelements which is not shared by their stable isotopes This misconception arises from two principal sources, differences of many orders of magnitude in the sensitivity of detection of stable and radioactive isotopes and excessive faith in the reported solubility products of slightly soluble compounds [29]

The controversy[30] as to whether radiocolloids are true colloids or merely radioactive ions adsorbed by impurities appears to STARIK[22] to be of purely historical interest To this writer it appears to be irrelevant

Nothing in the published literature refutes the concept of colloid formation as a precursor of precipitation or of surface adsorption as a substitute for and competitor with crystal growth Except at levels where the radiation significantly changes the composition of the solvent, the chemistry of stable and radioactive elements is the same

Residue adsorption provides another technique for studying the mechanism of precipitation at levels far below those at which stable isotopes are detectable

Acknowledgement The assistance of Mrs V A WURSTNER in carrying out many of the differential decay computations is gratefully acknowledged

M H KURBATOV and J D KURBATOV, *J Amer Chem Soc* **69**, 438 (1947)
H H SELIGER and A SCHWEBEL, *Nucleonics* **12**, No 7 54 (1954)
M HAISSINSKY *Acta Physiochem* (URSS) **3**, 517 (1935)
G K SCHWEITZER and W M JACKSON *J Chem Educ* **29**, 513 (1953)

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 501 to 506. Pergamon Press Ltd. Printed in Northern Ireland

THE DENSITY OF LIQUID BISMUTH FROM ITS MELTING POINT TO ITS NORMAL BOILING POINT AND AN ESTIMATE OF ITS CRITICAL CONSTANTS*

J. A. Cahill and A. D. Kirshenbaum
Research Institute, Temple University, Philadelphia

(Received 14 June 1962)

Abstract—The density of liquid bismuth was determined by the immersed sinker method from its melting point 544.5°K to its normal boiling point 1832°K with a probable error of 0.013 g/cm³. The density vs. temperature relationship may be expressed by the linear equation

$$D\,\mathrm{g/cm^3} = 10.665 - 11.820 \times 10^{-4}\,T$$

where T is in °K. The density of liquid bismuth is 10.022 g/cm³ at its melting point and 8.498 g/cm³ at its normal boiling point. The change in volume on melting was found to be −3.29 per cent of the solid volume. Molar volumes, atomic volumes and cubical expansion coefficients were calculated.

The critical constants of bismuth are estimated to be as follows:

$$T_{\mathrm{crit}} = 4620 \pm 460\,\mathrm{°K}$$
$$D_{\mathrm{crit}} = 2.60 \pm 0.3\,\mathrm{g_m/cm^3}$$
$$\mathrm{At\ Vol}_{\mathrm{crit}} = 80 \pm 8\,\mathrm{cm^3/gm}$$

PRESENT information available concerning the density of liquid metals at high temperatures is generally confined to relatively narrow temperature ranges near their melting points. The determination of densities over the whole normal liquid range i.e., from melting point to boiling point decreases the uncertainties created when one extrapolates present density data to higher temperatures. The reliability gained by the experimental determination over the entire normal liquid range is especially necessary to any one interested in predicting properties between the boiling point and critical point by the method recently outlined by GROSSE.(1,2)

The density of liquid bismuth has been reported by several investigators (See Table 5) who agree within 0.5 per cent of each other over the temperature range investigated. However the authors did not feel that a sufficient amount of the liquid range between the melting point and boiling point have been covered and therefore have measured the density of liquid bismuth from its melting point, 544.5°K to its boiling point, 1832°K by the Archimedean method.

EXPERIMENTAL

Apparatus and procedure

The carbon tube furnace and graphite apparatus used was described previously.(3,4) The Archimedean Method, described previously,(3,4) was used over the normal whole liquid range from the melting point to the normal boiling point. The maximum pressure bubble method(5) was used as a check at 630°K (boiling point of Hg). In the Archimedean method the liquid bismuth was refluxed at atmospheric pressure for ½ hr in order to remove all entrapped and dissolved gases. In these studies the volume of the sinker was always corrected for thermal expansion to operating temperature. The weight losses of the sinker were always corrected for surface tension using the data reported by Hogness[6] and Bircumshaw[7] extrapolated to 0 dynes/cm at the estimated critical temperature (4620°K). The surface tension correction varied from 0.5 per cent of total buoyancy (~35 g) at 600°K to 0.3 per cent at 1800°K.

---

* This work was supported by the National Science Foundation under grants 15540 and 18829.

[1] A. V. GROSSE, *J. Inorg. Nucl. Chem.* **22**, 23 (1961).

[2] A. V. GROSSE, Paper No. 2159, American Rocket Society, Space Flight Report to the Nation, New York (1961).

[3] A. D. KIRSHENBAUM, J. A. CAHILL and A. V. GROSSE, *J. Inorg. Nucl. Chem.* **22**, 33 (1961).

[4] A. D. KIRSHENBAUM, J. A. CAHILL and A. V. GROSSE, *J. Inorg. Nucl. Chem.* **24**, 333 (1962).

[5] A. D. KIRSHENBAUM and J. A. CAHILL, Transactions Quarterly A.S.M. **55**, 849 (1962).

Temperature reading

The temperature measurements were obtained by means of a calibrated copper-constantan thermocouple for temperatures below 1200°K and a calibrated optical pyrometer for temperatures above 1200°K.

The pyrometer was calibrated by measuring the melting points of platinum (2043°K) and silver (1234°K) and the boiling points of lead (2024°K) and silver (2510°K) at 760 mm pressure. The maximum deviation of any of these points was ±10°K.

A temperature reading of 1816 ± 15°K at 760 mm Hg pressure was observed with the optical pyrometer while the bismuth was boiling. This compares favourably with the best or most reliable literature value of 1832°K.[8]

Material used

The bismuth used in these studies (J. T. Baker Reagent) has the following impurities: 100 p.p.m. Sb, 50 p.p.m., each of Ag, Pb and Zn, 20 p.p.m. Fe, 10 p.p.m. Cu, 0.5 p.p.m. As. The remaining impurity was 220 p.p.m. (0.022 per cent) bismuth oxide. Since the measurements were made in graphite crucibles at elevated temperatures, the oxide was reduced to the metal. Therefore the metal had a purity of 99.972% Bi.

It has been reported by Ruff and Bergdahl[9] that the solubility of graphite in liquid bismuth is as follows:

°K	Wt. % C
1658	0.012
1681	0.018
1832	0.023

Samples were taken during each run and analyzed for % C. The values found agreed with those reported by Ruff and Bergdahl. Therefore a correction of 0.0034 g/cm³ was required at the boiling point and proportionately lower corrections at lower temperatures.

RESULTS

The liquid density values obtained from the studies show a straight line relationship when plotted against temperature and are shown in Fig. 1 together with the results of other investigators. The equation of the line as determined by the method of least mean squares is

$$D(\mathrm{g/cm^3}) = 10.665 - 11.820 \times 10^{-4}\, T(^\circ\mathrm{K}) \pm 0.013\ \mathrm{g/cm^3}$$

The values calculated from the above equation are compared with the experimental values in Table 1. The liquid density is 10.022 g/cm³ at the melting point (544.5°K) and 8.498 g/cm³ at the boiling point (1832°K). This is equivalent to a change in liquid density with temperature (dD/dT) of 11.820 × 10^{-4} g cm^{-3} °K^{-1}.

---

[6] T. Hogness, *J. Amer. Chem. Soc.* **43**, 1621 (1921).

[7] L. L. Bircumshaw, *Phil. Mag.* **3**, 1286 (1927).

[8] D. R. Stull and G. C. Sinke, *Advances in Chemistry Series*, Vol. 18, p. 55. American Chemical Society, Washington, D.C. (1956).

[9] O. Ruff and B. Bergdahl, *Z. Anorg. Chem.* **106**, 91 (1919).

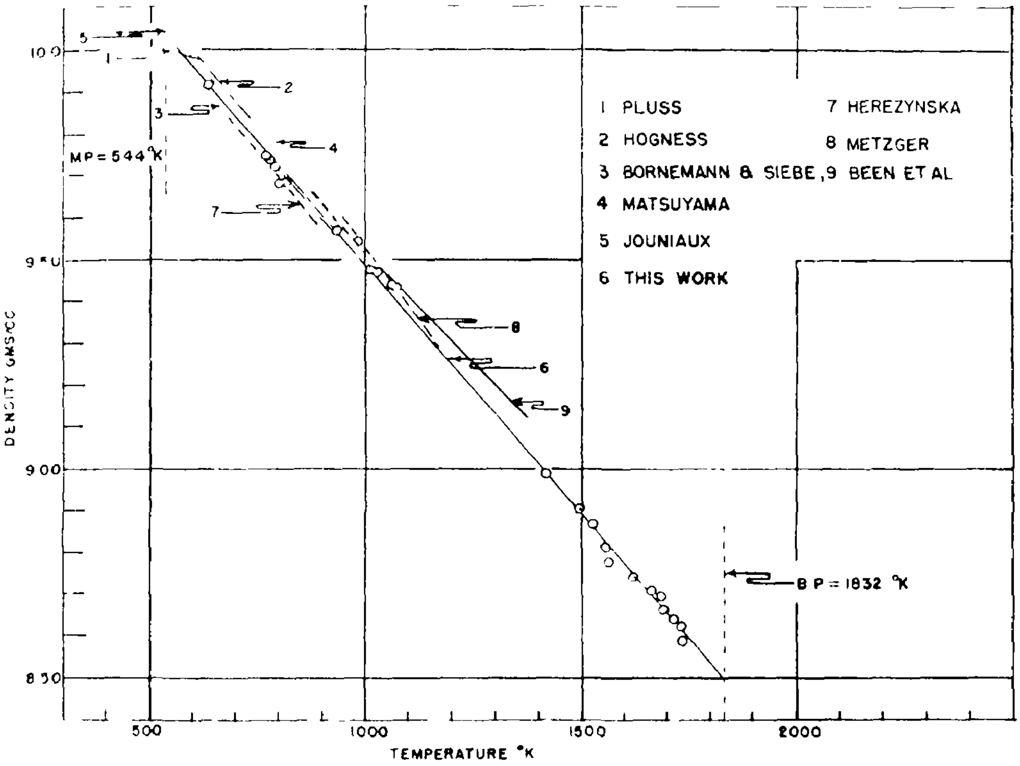


FIG. 1

Using a density of 9.785 g/cm³ calculated from X-ray data[10] at 293 K and thermal expansion coefficients reported by Cave and Holroyd[11] a value of 9.680 g/cm³ was obtained for the solid density at the melting point 544 K. Since the liquid density at the melting point is 10.022 g/cm³, the volume change on fusion ($\Delta V/V_s$) is −3.28 per cent.

Atomic and specific volumes were calculated for various temperatures using smoothed density values from the least squares equation. They are summarized in Table 2 together with cubical expansion coefficient values calculated from the equation

$$\frac{dD}{dT} = -\beta D_T$$

where dD/dT is the change of density with temperature, β is the cubical expansion coefficient and D_T is the density at temperature, T.

ESTIMATE OF CRITICAL CONSTANTS

Methods for estimating the critical constants of metals have recently been described by Grosse[1,2]. If reliable density data are available the critical density and critical pressure may be estimated by use of the law of rectilinear diameters. Alternatively the critical temperature of metals can be estimated by using entropy of vaporization data and applying the law of corresponding states. By employing these methods the

---

[10] Clark, *Applied X-rays* (3rd Ed.), p. 327. McGraw-Hill, New York (1940).

[11] F. Cave and L. V. Holroyd, *J. Appl. Phys.* **31**, 1357 (1960).

TABLE 1. DENSITY OF LIQUID BISMUTH

Temperature (°K)	Density (g/cm³) Exp	Calc	Exp – Calc
630	9.926	9.921	0.005
630	9.933	9.921	0.012
630	9.922	9.921	0.001
770	9.744	9.755	0.011
781	9.728	9.742	0.014
794	9.713	9.727	0.014
805	9.686	9.704	0.018
812	9.684	9.706	0.022
883	9.620	9.622	0.002
933	9.566	9.563	0.003
981	9.530	9.510	0.020
1011	9.476	9.470	0.006
1018	9.480	9.466	0.014
1027	9.480	9.457	0.023
1066	9.431	9.415	0.016
1073	9.423	9.402	0.021
1415	8.985	8.993	0.008
1493	8.902	8.901	0.001
1526	8.862	8.862	0.000
1553	8.806	8.830	0.024
1562	8.795	8.819	0.024
1625	8.742	8.745	0.003
1665	8.709	8.699	0.010
1687	8.688	8.672	0.016
1695	8.662	8.662	0.000
1716	8.644	8.637	0.007
1730	8.624	8.621	0.003
1730	8.599	8.621	0.022

TABLE 2. DENSITY, SPECIFIC VOLUME, ATOMIC VOLUME AND VOLUME COEFFICIENT OF EXPANSION OF LIQUID BISMUTH

Temperature (°K)	Density (g/cm³)	Specific volume (cm³/g)	Atomic volume (cm³/g atom)	Vol. Coef. of Expan. $\beta \times 10^6$ (°K^{-1})
544 (m.p.)	10.0218	0.09978	20.85$_0$	117.94
600	9.956	0.10044	20.99$_3$	118.72
800	9.719	0.10289	21.50$_4$	121.62
1000	9.483	0.10545	22.04$_0$	124.64
1200	9.247	0.10814	22.60$_1$	127.83
1400	9.010	0.11099	23.19$_7$	131.19
1600	8.774	0.11397	23.82$_0$	134.72
1800	8.537	0.11714	24.48$_2$	138.46
1832 (b.p.)	8.500	0.11765	24.58$_9$	139.06

critical temperature of bismuth was calculated to be 4620 ± 460 K while the critical density and atomic volume were 2.6 ± 0.3 g/cm³ and 80 ± 8 cm³/g atm respectively.

Liquid densities above the boiling point calculated from the rectilinear diameter and vapor pressure data[8] are tabulated in Table 3.

TABLE 3 — LIQUID DENSITY OF BISMUTH ABOVE ITS NORMAL BOILING POINT

Temperature (K)	Density (g/cm³)
2000	8.30
2500	7.69
3000	7.05
3500	6.38
4000	5.7
4500	4.9

DISCUSSION OF LITERATURE DATA AND COMPARISON WITH THIS WORK

A complete literature survey of the data on liquid bismuth is given in Table 4 together with a comparison of the densities at the melting point and the temperature

TABLE 4 — COMPLETE LITERATURE DATA ON THE DENSITY OF LIQUID BISMUTH (ARRANGED IN CHRONOLOGICAL ORDER)

Author	Year	Temperature range (K) From To	Range	Liquid density at melting point 544 K	dD/dT g cm^{-3} K^{-1} 10^{-4}	Method used	Reference
VICENTINI and OMODEI	1888	544	0	10.004			18
APRI	1914	573–773	200	9.99	6.36	-	19
PLUSS	1915	555 638	82	10.00	3.9	Archimedean principle	13
HOGNESS	1921	593–745	152	10.07	12.5	U-Tube pressure	6
BORNEMANN and SIEBE	1922	544–1073	529	10.030	11.96	Pycnometer	15
MAJIMA	1924	544	0	10.002	-		20
MATUYAMA	1929	548–923	375	10.066	12.70	Pycnometer	16
JOUNIAUX	1932	558–1350	792	10.04	11.53	Archimedean principle	12
BEEN *et al*	1950	573–1235	662	10.09	13.2		21
METZGER	1959	1073–1273	200	9.99	13.80	Bubble method	14
HERLZYNSKA	1960	573–873	300	10.012	12.38	Pycnometer	17
This work	1962	544 1832	1288	10.022	11.82	Archimedean principle	-

---

[12] A JOUNIAUX, *Bull Soc Chim France*, **51**, 677 (1932)

[13] M PLUSS, *Z Anorg Chem*, **93**, 1 (1915)

[14] G METZGER, *Z Phys Chem*, **211**, 1 (1959)

K BORNEMANN and P SIEBE, *Z Metallkunde*, **14**, 329 (1922)

[16] Y MATUYAMA, *Sci Rep Tohoko Imp Univ*, 1st Ser **18**, 19 (1929)

[17] I HERLZYNSKA, *Z Naturwissenschaften*, **47**, 200 (1960)

[18] G VICENTINI and D OMODEI, *Atti Accad Torino* **23**, 38 (1888)

[19] R APRI, *Intern Z Metallographie* **5**, 142 (1914)

[20] MAJIMA, *Bull Intern Phys Chem Res Japan* **3**, 61 (1924)

S A BEEN, H S EDWARDS, C E TEETER, JR and V P CALKINS, Report N E P A 1585 September 7 (1950) coefficients. The values are also plotted in Fig. 1. There is good agreement among the authors. Their average melting point value equals that found in this work, namely 10.022 g/cm³. Four independent methods were used, i.e.

(1) The Archimedean principle (this work, JOURNIAUX[12] and PLUSS[13])

(2) the U-tube pressure method (HOGNESS[6])

(3) the maximum bubble pressure method (METZGER[10]) and

(4) the pycnometer method (BORNEMANN and SIEBE[15], MATUYAMA[16] and HERCZYNSKA[17])

There is some disagreement in the temperature coefficients reported by the various investigators (3.9–13.8 × 10^{-4}). If the values of PLUSS, APRI and METZGER are disregarded since they are only over very short temperature ranges (∼200°), there is fairly good agreement among the remaining values (11.53–13.20 × 10^{-4}). The differences in temperature coefficients are mainly due to the measurement being made over relatively short temperature range (from 200 to 800°). The average of these values, 12.38 × 10^{-4} g/cm^{-3} K^{-1}, compares favorably with our value of 11.82 × 10^{-4} g/cm^{-3} K^{-1} obtained over the whole normal range (1290°).

Acknowledgements—The authors wish to thank Dr. A. V. GROSSE for his fruitful suggestions and to Mrs. I. STRENG for the carbon analysis of the bismuth samples.

J. Inorg. Nucl. Chem. 1963, Vol. 25, pp. 507 to 511. Pergamon Press Ltd. Printed in Northern Ireland

ADDUCTS OF BIS(2,4-PENTANEDIONO)-COPPER (II) WITH PYRIDINE BASES. STABILITY CONSTANTS AND HEATS OF REACTION

W. R. MAY* and M. M. JONES†
Department of Chemistry, Vanderbilt University, Nashville, Tennessee

(Received 5 July 1962; in revised form 22 October 1962)

Abstract—Co-ordination equilibria involving bis(2,4-pentanediono)-copper (II) and eight pyridine bases have examined spectrophotometrically at 20, 35 and 50°C. The heats of reaction, in benzene solution, for these same systems have also been determined in a solution calorimeter. The complexes formed are relatively weak ones and show no obvious correlation of stability constant with the electron releasing or withdrawing nature of the substituents. The heats of formation decrease in a nearly regular fashion as the electron withdrawing power of the substituents increases but reaches a nearly steady value for the most powerful of these groups. From this evidence and related data in the literature, it is suggested that correlation of ligand base strength and complex stability will not be found in very weak complexes. For these materials, solvation and steric effects will be of considerable relative importance and may overpower weak electronic effects.

PREVIOUS studies in this laboratory of complexes between copper (II) and aromatic carboxylates indicated that the relation between ligand basicity and complex stability could be of an inverse sort.[1] The present work was undertaken to extend these studies to complexes between pyridine bases and copper (II) in a different co-ordination environment. It was also considered desirable to select a system which was amenable to a concurrent calorimetric investigation. The pyridine base adducts with bis(2,4-pentanediono) copper (II) were selected for this study on the basis of previous work of GRADDON and WATTON.[2] These reactions are of the type given below, where B represents a molecule of base.

$$Cu(C_5H_7O_2)_2 + B \rightleftharpoons Cu(C_5H_7O_2)_2B$$

EXPERIMENTAL

The bis(2,4-pentanediono)-copper (II) was obtained from the MacKenzie Chemical Works, Central Islip, Long Island, New York. It was purified by recrystallization from chloroform prior to use. During the course of the experimentation, two further quantities were prepared. The first was subjected to a carbon and hydrogen analysis with the following results. (Found: C, 45.45; H, 5.34. Calc. for $Cu(C_5H_7O_2)_2$, C, 45.89; H, 5.40%.) The second quantity was analysed by electrodeposition of copper, with the following results. (Found: 24.18. Calc. for copper (II): 24.27%.) The pyridine derivatives were obtained from commercial sources and were purified by either recrystallization or distillation prior to use. Reagent grade benzene (Allied Chemical Co.) was redistilled before use.

---

* Abstracted in part from a thesis submitted to the faculty of the Graduate School of Vanderbilt University in partial fulfillment of the requirements of the degree of Doctor of Philosophy in Chemistry.

† To whom correspondence concerning this work should be sent.

[1] W. R. MAY and M. M. JONES, *J. Inorg. Nucl. Chem.* **24**, 511 (1962).

[2] D. P. GRADDON and E. C. WATTON, *J. Inorg. Nucl. Chem.* **21**, 49 (1961).

The formation constants were determined spectrophotometrically using either a Cary Model 1 ... a Spectronic 20 spectrophotometer. Both of these were equipped with a thermostated cell hol... which was held at the required temperature by water from a constant temperature bath. The gen... procedure used was that of GRADDON and WATTON.[2]

The heats of reaction were determined in a solution calorimeter of the usual Dewer type which ... similar in design to one described by HOLLOWAY.[3] The temperature measuring system was modified to obtain greater sensitivity. A thermistor bridge (E. H. Sargent Co.) was used and the off-balance potential was fed to a recorder set to give full deflexion for a 1 mV signal. Rough calibration showed *that this corresponded to 0.00035 C per min. A heater was constructed which consisted of resistance wire wrapped about an asbestos coated glass rod immersed in a sealed glass tube filled with silicone oil. The heater resistance was measured on a Meuller Bridge and found to be 53.57 Ω at 25 C. The calorimeter was standardized electrically during each run using this electrical heater and a storage battery. The current was determined by the accurate measurement of the potential drop this suffered in passing through a standard resistance of 1.00001 Ω (Gray Instrument Co.) at 25 C.*

In a typical run, 450 ml of benzene solution of bis(2,4-pentanediono)-copper (II) (0.005 M) was placed in the calorimeter which was then placed in a constant temperature (25 C) bath. A pipette containing the base or base solution in benzene was also equilibrated with the bath. After 2 hr, the pipette was inserted in the calorimeter; a further 30 min was allowed for equilibration, and a constant heat of stirring (about 0.002 C per min) was attained. The contents of the pipette were then forced into the calorimeter and the temperature change was recorded. The electrical calibration was then carried out. The calibration allowed each heat of reaction to be compared directly with a known amount of electrical energy. This procedure was checked for reliability by measuring the heat of reaction of dilute sodium hydroxide solution (450 ml of 0.005 M) with dilute hydrochloric acid (11.20 ml of 0.1 M). A value of 13.51 ± 0.16 kcal/mole was found as the result of ten such determinations. The accepted value for this is 13.35 kcal/mole.[4] The measured recorder deflexions were also calibrated with the electrical heater and the relationship between the deflexion and the electrical energy was found to be linear to within 1 per cent. The actual heat changes were of the order of 5–10 cal for most of the reactions and the temperature changes were of the order of 0.01–0.03 C.

RESULTS

The formation constants of the adducts are presented in Table 1, together with their standard deviations. Each constant represents the average of five or six determinations.

GRADDON and WATTON[2] measured the formation constant of bis(2,4-pentanediono)pyridinecopper (II) in benzene at room temperature and obtained the value of 7.2. This work yielded the value 7.4 at 23°C, which compares very favourably with GRADDON and WATTON's data.

TABLE 1. FORMATION CONSTANTS

$Cu(C_5H_7O_2)_2 + B \rightleftharpoons Cu(C_5H_7O_2)_2B$ (in benzene)

	Adduct (B)	K_{20}	K_{35}	K_{50}
1	Pyridine	8.72 ± 1.32	6.57 ± 1.69	5.18 ± 1.01
2	3-Picoline	5.97 ± 0.54	3.84 ± 0.40	3.92 ± 0.32
3	4-Picoline	10.9 ± 0.69	8.75 ± 0.75	7.05 ± 0.74
4	4-Chloropyridine	5.65 ± 0.81	5.01 ± 0.57	4.17 ± 0.56
5	3-Cyanopyridine	6.83 ± 1.44	5.34 ± 1.79	4.63 ± 1.95
6	3-Acetylpyridine	10.3 ± 2.54	9.07 ± 1.44	7.65 ± 1.42
7	4-Benzoylpyridine	18.3 ± 6.13	15.4 ± 4.48	14.8 ± 3.97
8	3-Bromopyridine	5.02 ± 1.13	4.30 ± 0.70	3.81 ± 0.63

---

(3) J. H. HOLLOWAY, Thesis, University of North Carolina (1959).

(4) Circular 500, U.S. Bureau of Standards, Washington, D.C.

The calorimetric data is presented in Table 2 This includes the measured heats of solution or of dilution for the pyridine bases in benzene in solutions whose final concentrations were very close to those used in the complexation studies. The measured heats were composed of two parts, (1) the heat of solution (or dilution) of the unreacted ligand and (2) the heat of coordination The concentration of the complex was calculated from the known stability constant and from this the amount of unreacted ligand could be obtained The heat of solution of the unreacted ligand was then subtracted from the measured heat to obtain that heat change due to complexation Each of the calorimetric values is the average of at least three independent determinations

TABLE 2 THERMODYNAMIC CHANGES

	Adduct	ΔH_{soln} (cal/mole)	ΔH_r (kcal/mole)	ΔF (kcal/mole)	ΔS (e u)	$\Delta H_r{}^a$ (kcal/mole)
1	Pyridine	27.5 ± 1.6^b	6.05 ± 1.03	1.21	16.2	3.31
2	3-Picoline	122.0 ± 27^b	8.04 ± 0.86	0.93	23.9	−3.38
3	4-Picoline	104.0 ± 8.5^b	11.5 ± 0.53	1.35	34.2	−2.71
4	4-Chloropyridine	74.3 ± 4.8^c	0.66 ± 0.52	1.00	1.12	−2.11
5	3-Cyanopyridine	214.0 ± 19^d	2.50 ± 0.41	1.08	4.77	2.92
6	3-Acetylpyridine	172.0 ± 15^e	-1.76 ± 0.49	1.35	1.38	1.73
7	4-Benzoylpyridine	0.0 ± 0^f	1.42 ± 0.34	1.68	0.87	1.30
8	3-Bromopyridine	121.0 ± 30^g	1.62 ± 0.66	0.90	−2.42	−2.17

a These values are calculated from the temperature variation of the equilibrium constants
b These values are for an integral heat of solution
c–g These values are for heats of dilution with the following concentration changes
c 5.709 M to 0.1390 M
d 3.584 M to 0.08726 M
e 5.271 M to 0.1283 M
f 0.8007 M to 0.01956 M
g 4.598 M to 0.1144 M

DISCUSSION

It can easily be seen that the equilibrium constants for this reaction are not affected by substituent groups in the manner anticipated from their established electron releasing or withdrawing properties Use of JAFFE's(5) sigma values for the substituent constants shows very definitely that the stability constants cannot be correlated quantitatively by a relationship such as the Hammett equation This is the situation which has been found in other systems, such as the sulphonate complexes of cadmium (II) (6) In situations in which a correlation has been found between the stability constant and the ligand structure in adduct formation reactions similar to the type studied here, the free energy changes were much greater than found here For example the free energy changes varied from −4 to 8 kcal/mole for the addition of an alkyl amine to diacetylbisbenzoylhydrazinonickel (II) (7–10) In this work, the

---

H H JAFFE, *Chem Rev* **53**, 191 (1953)
J F TATE and M M JONES, *J Amer Chem Soc* **83**, 3024 (1961)
L SACCONI, G LOMBARDO and R CIOFALO, *J Amer Chem Soc* **82**, 4182 (1960)
L SACCONI, G LOMBARDO and P PAOLETTI, *J Amer Chem Soc* **82**, 4185 (1960)
L SACCONI and G LOMBARDO, *J Amer Chem Soc* **82**, 6266 (1960)
L SACCONI *Ricerca Sci* **30**, Suppl No 5, 89 (1960)

free energy changes varied from 0 900 to 1 68 kcal/mole It would appear that effects due to solvation or steric interaction overpower the relatively small electronic effects

Since the reactions were carried out in a non-coordinating solvent, the reactants were anhydrous and no displacement of ligands occurred during the reaction The heat of reaction is thus a direct measure of the heat evolved when the base adds to the complex Therefore the heat of reaction should be very similar to the energy of the new co-ordination bond which is formed To analyse the effects of the change of structure of the base on the heat of reaction the heat of reaction was plotted against

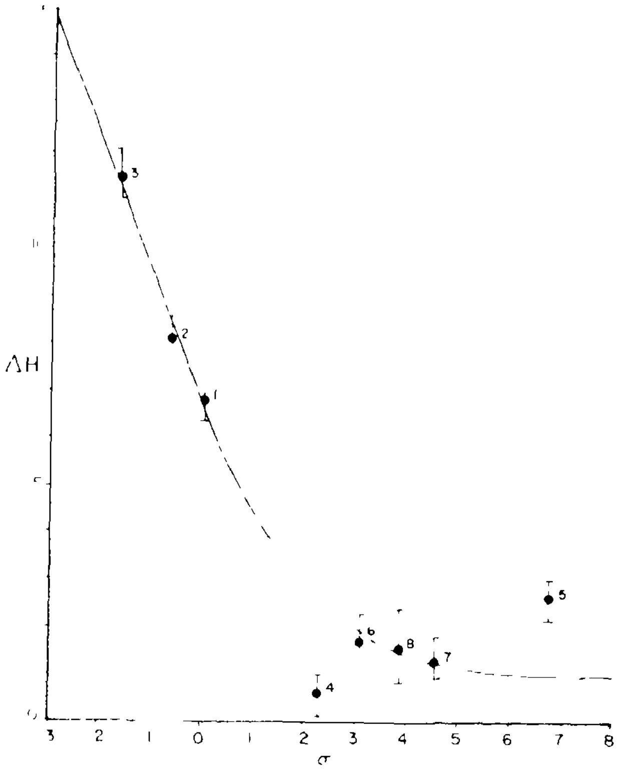
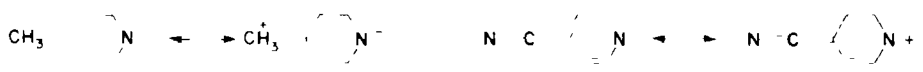


FIG 1 —Variation of the enthalpy of complexation with the sigma values of the ligand substituents ΔH is in kcal mole The compounds are numbered as in Table 2

the Hammett sigma constant in Fig 1 A definite trend is seen in which the heat of reaction is rather high for the stronger bases and decreases toward a limiting value as the basicity decreases

This behaviour may be explained by examining the importance of the various canonical forms possible for pyridine and pyridine derivatives Structures I, II, III and IV demonstrate the canonical forms possible for pyridine with an electron donating group such as the methyl group and an electron withdrawing group such as



I II III IV

the cyano group Through the comparison of the dipole moments of a series of pyridine derivatives and the corresponding benzene derivatives, it was found that the electron donating groups have a large effect on increasing the electron density on the pyridine nitrogen whereas the electron withdrawing groups have approximately the same effect regardless of the electron withdrawing power of the substituent (11) Thus, the stronger bases are able to force a pair of electrons into the d_{z^2} orbital of the square planar copper (II) complex with a corresponding higher heat of reaction However, the electron withdrawing groups reduce the basicity of these ligands to a common level with a corresponding reduction of the heat of reaction until a constant value is obtained

Considering the heat of reaction to approximate the bond energy of the new co-ordinate bond, the bond energy is found to increase in the following order 4-chloropyridine ~ 4-benzoylpyridine ~ 3-acetylpyridine ~ 3-bromopyridine < 3-cyanopyridine pyridine 3-picoline 4-picoline This order very nearly follows the order of basicity of the bases

The entropy changes also follow the decrease in basicity of the ligand species A negative entropy change is expected any time the reaction involves the reduction of the number of free particles, the number of degrees of independent motion of the species or the degree of randomness The comparatively large negative entropies for the pyridine, 3-picoline, 4-picoline and 3-cyanopyridine indicate definitely this is the situation The very low positive values indicated for 4-chloropyridine and 4-benzoylpyridine are more difficult to rationalize The heat of reaction was very small for both cases leading to an increased error in the calculation of the entropy changes It is evident that the entropy changes for the reaction with the less basic derivatives of pyridine are very small

In conclusion, a relationship between the basicity of the ligand and the heat of reaction has been found to apply to the reaction being studied This work has also shown that the energy of the bond formed is very weak In comparison, the Cu–O bond in the bis(2,4-pentanediono) copper (II) complex is 48 7 kcal/mole (12)

Acknowledgement This work was carried out under a grant from the National Science Foundation whose assistance we wish to acknowledge with thanks

---

(11) R A Barnes in *Pyridine and Its Derivatives* (Edited by E Klingsberg) Part One, p 8 Interscience New York

(12) M M Jones, B J Yow and W R May, *Inorganic Chem* 1, 166 (1962)

J Inorg Nucl Chem, 1963 Vol 25 pp 513 to 518 Pergamon Press Ltd Printed in Northern Ireland

COMPLEXES OF THE LANTHANIDE ELEMENTS WITH MERCAPTOCARBOXYLATE LIGANDS

J L Bear, G R Choppin and J V Quagliano
Department of Chemistry, Florida State University, Tallahassee, Florida

(*Recieved* 13 *August* 1962)

Abstract —Stability constants have been determined by the Bjerrum method for complexes of the α-mercaptopropionate, β-mercaptopropionate and S-ethylthioglycolate ions with yttrium (III) and several trivalent lanthanide ions The investigation indicates that the acid anions function as monodentate ligands

THE two primary factors which determine the stability of complexes are the nature of the metal ion and the nature of the ligand Since the 4*f*-orbitals play very little or no role in bonding and the tripositive lanthanide ions have the same outer electronic configuration (i e , $5s^2\ 5p^6$), these metal ions exhibit the expected strong similarities with each other in the stability of their complexes The major difference in the stability constants for any particular ligand might be expected to be due to the increase in acidity of the metal ion through the series from lanthanum to lutetium resulting from the lanthanide contraction Complexes with various polycarboxylic acid ligands,(1 2 3 4) such as EDTA, and α-hydroxycarboxylate ligands,(5,6) such as glycolate, show an increase in stability from La to Lu in agreement with the increase in acidity. However, the trend is not uniform, usually showing a slight deviation around gadolinium

SONESSON(7) found that the lanthanide acetate complexes increase in stability with atomic number up to samarium, decrease in stability from gadolinium to dysprosium, and remain almost constant to lutetium This same trend was observed for the lanthanide complexes with α-mercaptoacetate ligand (8) Both ligands function as monodentate ligands, whereas the α-hydroxycarboxylate ions function as chelate ligands with these lanthanide metal ions Chelation increases the value of the successive stepwise stability constants by approximately a factor of five for glycolate relative to acetate In addition, the order of stability α-hydroxyisobutyrate > lactate > glycolate would seem to indicate that the inductive effect arising from methyl group substitution which increases the basicity of the hydroxyl group is more important than the steric effect of this substitution (6)

In the present investigation, the stepwise formation constants have been determined

---

(1) J Wheelwright, F H Spedding and G Schwarzenbach *J Amer Chem Soc* **75**, 4196 (1953)

(2) G Schwarzenbach, R Gut and G Anderegg, *Helv Chim Acta* **37**, 937 (1954)

(3) F H Spedding, J E Powell and E J Wheelwright, *J Amer Chem Soc* **78**, 34 (1956)

(4) R C Vickery, *J Chem Soc* 421, 1895 (1952)

(5) S Sonesson, *Acta Chem Scand* **12**, 1937-1954 (1958)

(6) G R Choppin and J Chopoorian, *J Inorg Nucl Chem*, **22**, 97 (1961)

(7) A Sonesson, *Acta Chem Scand* **12**, 165 (1958)

(8) J L Bear, G R Choppin and J V Quagliano, *J Inorg Nucl Chem* In press

for the complexing of several trivalent lanthanide ions and Y(III) with α-mercaptopropionate, β-mercaptopropionate and S-ethylthioglycolate ions. Our purpose was to learn if various changes in the nature of the ligand such as inductive effects, steric factors and chelate ring size would enhance metal–sulphur bond formation.

Determination of stability constants

The successive formation constants were calculated by the method of Bjerrum, as previously described by Choppin and Chopoorian for the complexes of the α-hydroxycarboxylic acids.(6)

The calculation of $\bar{n}$ and $[L]$

The concentration of the free ligand was calculated from hydrogen ion measurements, using a glass electrode as previously described.(8)

EXPERIMENTAL

Materials

Sodium perchlorate. G. F. Smith Co., anhydrous reagent grade was used as obtained in adjusting the solutions to 2.0 M ionic strength.

Lanthanide perchlorate solutions. These were prepared as described previously.[illegible]

α-mercaptopropionic acid buffer solution. The aqueous solution of α-mercaptopropionic acid (Eastern Chemical Co.) was standardized against sodium hydroxide. The buffer solution was prepared by partially neutralizing the standard acid solution with sodium hydroxide to a buffer ratio of unity. C_I' was 0.8009 M.

β-mercaptopropionic acid buffer solution. The acid was obtained from Eastern Organic Chemicals, and the solution prepared as above. C_I' was 1.1014 M.

S-ethylthioglycolic acid buffer solution. S-ethylthioglycolic acid was prepared by the general method described by Ramberg.(9) C_I' was 0.598 M.

Equipment

The glass and reference electrodes. The glass electrode was a Beckman Type "42". A silver–silver chloride reference electrode was used.

The pH meter. A Beckman model G was used.

The potentiometer. A Leeds-Northrup model K-3 potentiometer equipped with a Weston standard cell was used.

Procedure

Titrations were carried out as previously described.(8) The [H] and [H] were determined by titrating with the acid buffer respectively a solution of sodium perchlorate alone and a solution of sodium perchlorate containing metal ions.

RESULTS

Tables 1(a–b) list some of the experimental data and the calculated values of $[L]$ and $\bar{n}/[L]$. The values for $E' - E$ are calculated from e.m.f.'s measured during the titration.

The values obtained for the stability constants, listed in Table 2, were calculated from $\bar{n}$ and $[L]$ values using an iterative least squares method on an IBM 709 computer.(10) Errors were found to be of the order ± 10 per cent for K_1 and ± 30 per cent for K_2. Random computational errors gave such large fluctuations in the values of K_3 that no values can be confidently reported.

---

(9) L. Ramberg, *Ber. Chem. Dtsch. Ges.* **40**, 2588 (1907).

(10) J. A. Chopoorian, G. R. Choppin, A. C. Griffith and J. Chandler, *J. Inorg. Nucl. Chem.* **21**, 21 (1961).

TABLE 1 —DETERMINATION OF $\bar{n}/[L]$ FROM EXPERIMENTAL DATA

(a) Europium α-mercaptopropionate system

C_H^0 0.70 mM C_L^0 800.92 mM

C_M^0 - 18.06 mM μ 2.00 M

Volume of titrant (ml)	$(E' - E)$ (mV)	$[L]$ (mM)	$\bar{n}/[L]$ (M^{-1})
0.10	15.5	4.37	54.27
0.20	13.9	9.26	43.16
0.30	12.9	14.23	38.86
0.40	12.0	19.47	35.23
0.50	11.2	24.80	32.60
0.75	9.8	38.37	27.97
1.00	8.6	52.34	24.39
1.25	7.6	66.34	21.71
1.50	6.7	80.94	18.87
2.00	5.6	107.66	16.20
2.50	4.6	134.26	13.57
3.50	3.7	179.80	11.73
4.50	3.2	219.80	10.64

(b) Europium β-mercaptopropionate system

C_H^0 0.70 mM C_L^0 1101.4 mM

C_M^0 18.06 mM μ 2.00 M

Volume of titrant (ml)	$(E' - E)$ (mV)	$[L]$ (mM)	$\bar{n}/[L]$ (M^{-1})
0.10	27.1	3.80	106.66
0.20	22.4	9.06	78.83
0.30	20.6	14.41	70.35
0.40	19.1	20.17	63.63
0.50	17.8	26.26	58.14
0.75	15.0	42.88	47.22
1.00	12.8	60.89	39.30
1.25	11.4	78.58	34.75
2.00	8.4	132.44	25.66
2.50	7.4	165.22	23.07
3.00	6.4	198.14	20.34
3.50	5.8	227.41	18.91
4.00	5.3	256.10	17.74

TABLE 2

Ion	β-mercapto-propionate		α-mercapto-propionate		S-Ethylthio-glycolate	
	K_1	K_2	K_1	K_2	K_1	K_2
La	66	18	31	5	50	7
Nd	86	20	36	6	52	7
Sm	156	21	68	8	70	8
Eu	141	22	64	7	61	8
Gd	106	21	42	6	50	8
Tb	62	21	40	8	34	9
Ho	48	21	28	9	27	9
Er	50	24	24	11	26	10
Yb	56	21	27	10	25	10
Y			24	5	26	5

Plots of $\bar{n}/[L]$ vs $[L]$ for the α-mercaptopropionate and β-mercaptopropionate europium (III) systems are shown in Fig 1

DISCUSSION

A comparison of the stability constants for the lanthanide complexes with acetate, glycolate, and α-mercaptoacetate ligands indicated that the α-mercaptoacetate ion acts as a monodentate ligand There are two possible explanations for this Either the sulphur atom of this ligand is a poor donor for lanthanide ions, or the size of the sulphur atom creates sufficient steric hindrance to prevent formation of a five-membered chelate ring The α-mercaptopropionate ion has a more electronegative sulphur atom than the α-mercaptoacetate ion as a result of the methyl group on the α-carbon atom Therefore, the α-mercaptopropionate ion could show a greater tendency for the formation of the sulphur–metal bond However, the stability constants of the α-mercaptopropionate complexes are only slightly higher than those of the α-mercaptoacetate complexes This increase in stability is not large enough to be attributed to chelation, whereas it can be satisfactorily explained by the difference in acid strength between the α-mercaptoacetic acid and the α-mercaptopropionic acid The S-ethylthioglycolate complexes are slightly more stable than the α-mercaptopropionate complexes, but, again, this can be explained by the fact that S-ethylthioglycolic acid is slightly weaker than α-mercaptopropionic acid

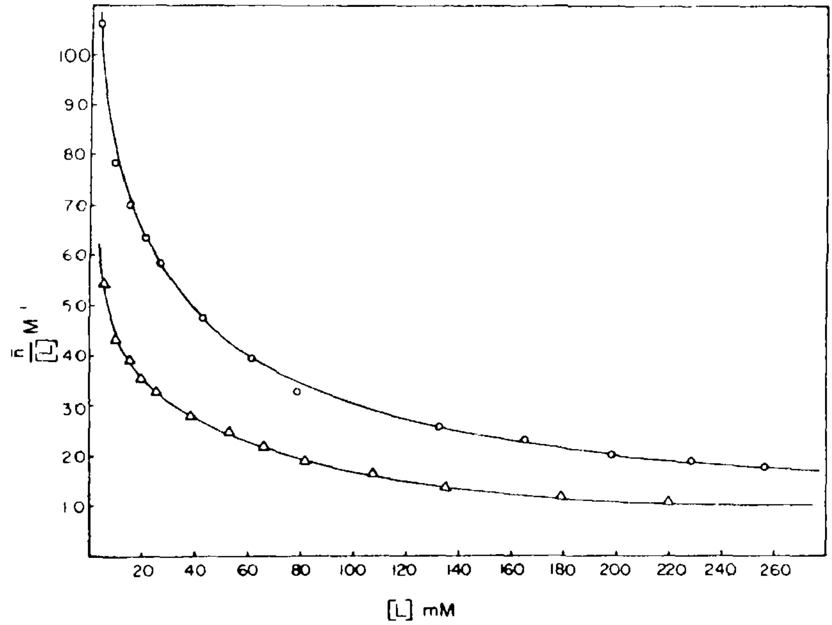


FIG 1 —$\bar{n}/[L]$ vs $[L]$ curves for systems listed in Table 1
○ Europium β-mercaptopropionate system
△ – Europium α-mercaptopropionate system

On the other hand, the β-mercaptopropionate complexes are considerably more stable Considering only the relative acid strengths, β-mercaptopropionate would be expected to form stronger complexes than α-mercaptopropionate and S-ethylthioglycolate but weaker complexes than acetate In Fig 2, log K_1 is plotted as a function of log K_a of the acids of these ligands The K_a values were determined by titration in a constant ionic strength medium of 2 0 M $NaClO_4$ The β-mercaptopropionate complexes lie above the line of the other ligands, which shows that their stability is greater than expected from the acid strengths alone Inasmuch as chelation by this ligand would involve a six-membered ring, it is attractive to consider that the increased stability reflects metal-sulphur bonding due to relief of steric effects by the larger ring size However, the increase in stability of the β-mercaptopropionate complexes is much less than that associated with increase in stability resulting from the chelation in glycolic acid It is necessary to obtain information on enthalpy and entropy of complexation before this question can be definitely answered Such measurements are in progress at present

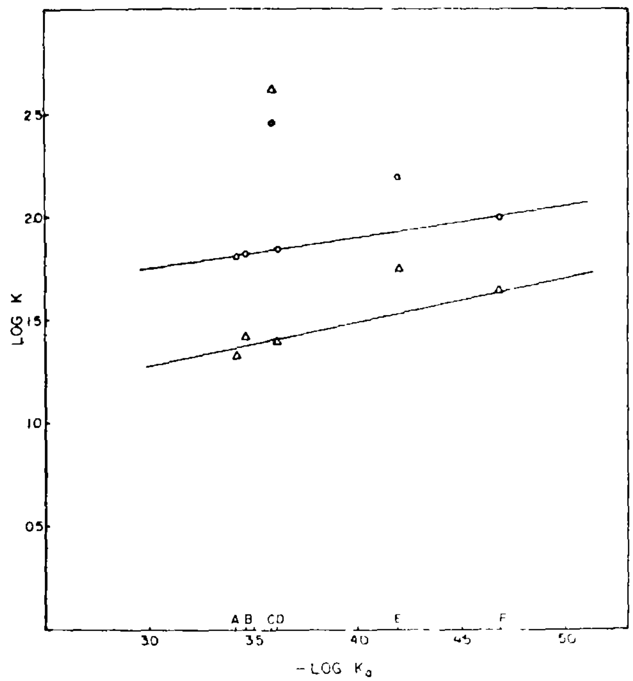


Fig 2 - Plot of log K_1 vs $-\log K_a$ for samarium (○) and ytterbium (△) complexes
A — mercaptoacetate
B = α-mercaptopropionate
C = glycolate
D = S-ethylthioglycolate
E = β-mercaptopropionate
F Acetate

The variation of the first stability constant, K_1, with atomic number is given in Fig 3 for the three ligand systems For all three ligands, the stability of the mono-ligand complex increases with atomic number from La to Sm, decreases from Sm to Eu and then remains rather constant for the remaining lanthanides This pattern is similar to that of K_1 for the acetate and α-mercaptoacetate complexes On the basis of the plot of K_1 vs the atomic number of the metal, it seems probable that all five acid anions behave as monodentate ligands This pattern would seem to be typical of the monodentate carboxylic acid complexes of the lanthanides Again, the explanation of this trend may be understood after the thermodynamic parameters are known

Stability constants of the complexes of α-mercaptoacetate and β-mercaptopropionate ligands with the lightest lanthanide ions have been reported by Cefola *et al* [11] Their values are considerably larger than our values, but this may be due to the difference in ionic strength between the two sets of experiments (0 1 M vs 2 0 M) The ratio of the K_1 values for lanthanum glycolate and β-mercaptopropionate from

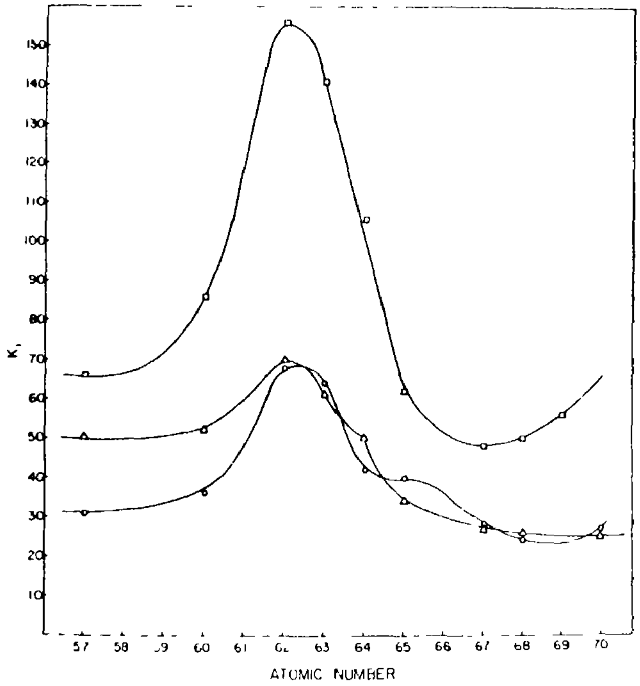


Fig. 3 —Plot of K_1 vs atomic number for lanthanide complexes
β-mercaptopropionate complexes
S-ethylthioglycolate complexes
α-mercaptopropionate complexes

both groups is about the same However, the ratio of K_1 values for glycolate and α-mercaptoacetate is larger in our measurements by a factor of three The reason for this variance is not known, however, Cefola points out that their titrations involved pH values as high as six which could result in high K_1 values due to hydrolysis of the lanthanide ions The fact that their values of K_2 exceed the K_1 values would add further weight to this as calculation of K_2 is much more sensitive to the higher pH range of the titration Their explanation for the higher K_2 values is dependent on the assumption of chelation which our data would indicate is not a valid assumption

Acknowledgements—The financial support of the U S Atomic Energy Commission is gratefully acknowledged We are indebted to Dr H Yoneda for his preparation of the S-ethylthioglycolic acid

[11] M Cefola, A S Tompa, A V Celiano and P S Gentile, *J Inorg Chem* **1**, 290-293 (1962)

J Inorg Nucl Chem 1963, Vol 25 pp 519 to 523 Pergamon Press Ltd Printed in Northern Ireland

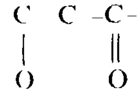
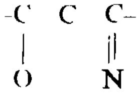
COMPLEX FORMATION BY N-SUBSTITUTED ACETOACETAMIDES—I

ACID DISSOCIATION CONSTANTS AND STABILITY CONSTANTS OF THE BERYLLIUM COMPLEXES

H J HARRIES
Chemistry Department, Derby and District College of Technology, Derby, England

(*Received* 5 *May* 1962, *in revised form* 21 *July* 1962)

Abstract A number of derivatives of acetoacetamide have been examined as chelating agents Using the glass electrode, the acid dissociation constants have been determined in 50 per cent dioxane (v/v) and the stability constants of their beryllium complexes measured The variation of pK_a with N-substituent is interpreted in terms of electronic and steric effects The variation of stability constants shows that the chelating power is related to the basic strength of the enolate ion for a series of structurally similar compounds

The complex-forming properties of β-diketones are well established(1) and stability constants have been related to acid strength of the chelating agent by several workers CALVIN and WILSON(2) and, more recently, VAN UITERT *et al* (3) have related basic character of the enolate ion to the formation of complexes containing the grouping  $\underset{\mathrm{O}}{\underset{|}{\mathrm{C}}}\ \ \mathrm{C}\ -\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}-$, while MARTIN *et al* (4) have made similar studies on the grouping  $-\underset{\mathrm{O}}{\underset{|}{\mathrm{C}}}\ \ \mathrm{C}\ \ \underset{\mathrm{N}}{\underset{\|}{\mathrm{C}}}-$ found in β-ketoimine complexes

The compounds chosen for the present study are ortho-substituted acetoacetanilides which are capable of the keto-enol tautomerism shown by acetylacetone Due to the low water solubility of these compounds and their metal chelates, the medium used was 50 per cent (v/v) dioxane

EXPERIMENTAL

pH Determinations pH determinations were made using a Cambridge pH mV Meter this being checked regularly against a standard Weston Cell The electrodes used were a wide-range glass electrode and a saturated Calomel electrode made up using 50 per cent dioxane as the solvent for KCl Temperature was maintained at 25 C ± 0 05° Calibration of the pH-meter was carried out as follows buffer solutions containing acetic acid and sodium acetate in 50 per cent dioxane were prepared Their pH values were calculated using an extrapolated value for pK_a of acetic acid (5) An activity correction was made using data available for hydrochloric acid in dioxane water mixtures (6) The plot of observed mV against calculated pH was linear, having a slope of 0.058 (theory value 0.059) and coincided with the graph obtained by plotting pH against mV for a range of aqueous buffers

---

(1) *Stability Constants, I-Organic Ligands* Chem Soc Special Publication No 6 (1958)

(2) M CALVIN and K W WILSON, *J Amer Chem Soc* **67**, 2003 (1945)

(3) L G VAN UITERT, W C FERNELIUS and B E DOUGLAS, *J Amer Chem Soc* **75**, 457 (1953)

(4) D F MARTIN, G A JANUSONIS and B B MARTIN *J Amer Chem Soc* **83**, 73 (1961)

(5) B E CONWAY, *Electrochemical Data*, p 196 Elsevier (1952)

(6) H S HARNED and B B OWEN, *The Physical Chemistry of Electrolytic Solutions*, p 548 Reinhold, New York (1950)

Dioxane The solvent was purified using the method recommended by Weissberger and Proskauer[7]

Chemicals B D H reagents were used throughout, except the pyridine derivative which was obtained from Newton-Maine Ltd These were recrystallized to give literature melting points Beryllium sulphate of at least 99 per cent purity was used

Acid dissociation constants These were determined by titration of M/2 NaOH against M/10 solutions of the chelating agents The pH at half-neutralization was taken as pH = pK_a This gives comparative values, that is they are not true thermodynamic constants This procedure was adopted because (a) extrapolation to zero concentration was subject to large errors in cases where this was attempted and (b) the calculation of activity corrections was not possible for the enolate ion due to lack of suitable data

pH Titrations Solutions containing perchloric acid, beryllium sulphate and a two- to fivefold excess of chelating agent in a total volume of 100 ml were titrated with M/2 NaOH in 50 per cent dioxane

Calculation of results The method used was based on that of Bjerrum[8]

Let C_M total concentration of metal salt,

Let C_{HC} total concentration of chelating agent,

A concentration of perchloric acid

Then, assuming that the divalent metal forms a 1:2 chelate via the 1:1 chelate, whose stability constants are K_1 and K_2 respectively, the following equations may be derived

$$C_M = [M^{2+}] + [MC^+] + [MC_2] \qquad (1)$$

$$C_{HC} = [HC] + [C^-] + [MC^+] + 2[MC_2] \qquad (2)$$

$$[H^+] + 2[M^{2+}] + [MC^+] + [Na^+] = [OH^-] + [ClO_4^-] + 2[SO_4^{=}] + [C^-] \qquad (3)$$

Total bound chelating agent = $[MC^+] + 2[MC_2]$

Using equations (1)–(3), it can be shown that

$$[MC^+] + 2[MC_2] = [Na^+] + [H^+] - A - [OH^-] - \frac{K_a}{[H^+]}\{C_{HC} + A + [OH^-] - [Na^+] - [H^+]\} \qquad (4)$$

The value of K_W used to calculate $[OH^-]$ was extrapolated from data given by Conway[6] ($\log k_W = -16.1$)

The average number of chelate groups bound per metal ion ($\bar{n}$) is given by

$$\bar{n} = \{[MC^+] + 2[MC_2]\}/C_M$$

$\bar{n}$ can then be calculated from (4) (2) gives a value for $\{[HC] + [C^-]\}$ which, in conjunction with K_a, enables $[C^-]$ to be calculated

$$[C^-] = \frac{K_a}{K_a + [H^+]}\{[HC] + [C^-]\}$$

From a plot of pC ($= -\log [C^-]$) against $\bar{n}$ can be obtained values of K_1 and K_2 Log K_1 and log K_2 are given by the values of pC corresponding to $\bar{n} = 0.5$ and $\bar{n} = 1.5$ respectively[8]

RESULTS AND DISCUSSION

The values of pK_a, log K_1, log K_2 and log β_2 ($=$ log K_1K_2) are given in Table 1 The stability constants given are those obtained for a starting solution containing $C_M = 10^{-3}$ M, $C_{HC} = 5 \times 10^{-3}$ M and $A = 5 \times 10^{-3}$ M Experiments were carried out using concentrations up to ten times those given and varying the excess of chelating agent These gave slightly larger values of K_1 and K_2 Generally, the difference was not greater than 0.1 log units although a few results were up to 0.3 log units high

---

[7] A Weissberger and E S Proskauer, *Technique of Organic Chemistry*, Vol 7, p 371 Interscience New York (1955)

[8] J Bjerrum, *Metal Ammine Formation in Aqueous Solution* p 35 Haase, Copenhagen (1941)

(It was estimated that the experimental technique limited the accuracy of the final results to ±0.05 log units, the further variations noted are considered to be due to variation of activities. It can also be shown that calculation of K_1 and K_2 from

TABLE 1.—ACID DISSOCIATION CONSTANTS OF $CH_3CO\,CH_2\,CO\,NH\,R$ AND STABILITY CONSTANTS OF THE BERYLLIUM COMPLEXES

Compound No.	R	pK_a	$\log K_1$	$\log K_2$	$\log \beta_2$
1	2,5-dichlorophenyl-	10.2	6.7	5.4	12.1
2	2-pyridyl-	10.6	7.8	6.65	14.45
3	2-chlorophenyl-	10.65	7.4	6.2	13.5
4	2-tolyl-	11.3	7.9	6.6	14.5
5	2-methoxyphenyl-	11.4	8.1	6.9	15.0
6	phenyl-	11.6	8.3	7.0	15.2
7	acetylacetone	10.3	8.3	7.4	15.7
8	ethyl acetoacetate	11.9	8.6	7.6	16.2

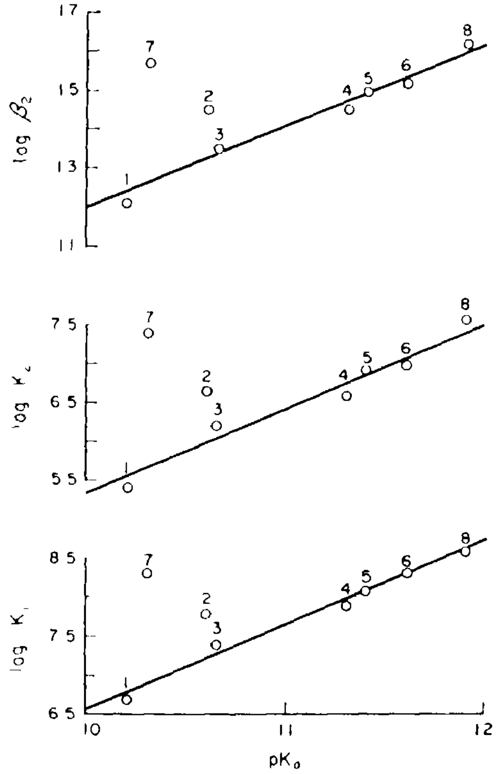


FIG. 1.—Relation between acid dissociation constant of chelating agent and stability of beryllium complex. Numbers 1–8 correspond to the compounds shown in Table 1.

experimental results was most sensitive to small errors in pH or errors due to acid impurities in the reagents in systems involving high concentrations and large excesses of chelating agent. This would affect the results in the way noted.) Fig. 1 shows plots of pK_a against $\log K_1$, $\log K_2$ and $\log \beta_2$.

Variation of pK_a The acid dissociation of the enol form of these compounds is favoured by low electron density in the region of the C--O links which is, in turn, enhanced by electron withdrawal in the direction of the aromatic ring The electron-withdrawing abilities of the ring substitutuents is known to be $-\mathrm{OCH}_3 < -\mathrm{CH}_3$ $-\mathrm{H}$ < $-\mathrm{Cl}$ and would lead to the conclusion that this would be the order of the acid dissociation constants These results indicate that the H-compound is apparently anomalous This may be explained with the aid of Fig 2 The electron withdrawal by X is reduced by ring formation due to hydrogen bonding When X is H, the two rings may be co-planar and thus form an extended conjugated system, whose stability is thereby increased When X is larger than H, steric interference no longer allows coplanarity and the enhanced stability of the H-bonded ring is no longer possible This effect is parallel to that shown in the case of the ortho-substituted benzoic acids whose acid dissociation constants decrease in the order Cl > CH_3 OCH_3 > H (9) The variation in both cases is due to a combination of (a) the electronic effects of the substitutuents and (b) the steric effect of substitution in the ortho-position

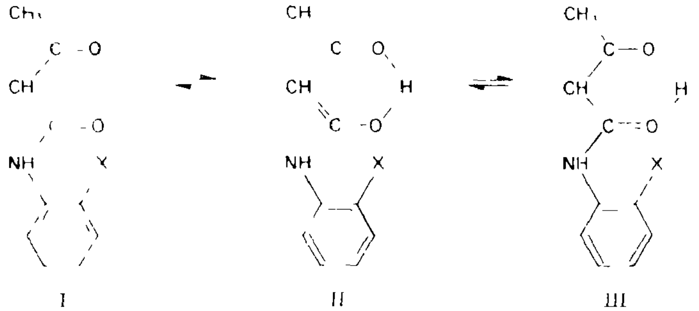
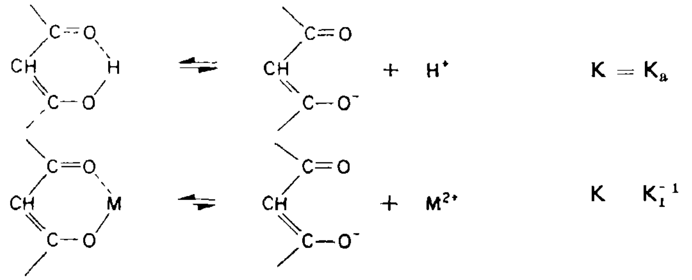


FIG 2 Keto-enol tautomerism in substituted acetoacetanilides

Variation of stability constants It can be seen, from Fig 1, that the chelating ability increases with the basic strength of the enolate ion This applies to a series of structurally similar compounds This is in accordance with the findings of CALVIN and WILSON(2) who found that different series of chelating agents gave a series of parallel lines for pK_a/log K plots The linearity is not unexpected in view of the similarity between the two reactions For a structurally similar series, the entropy of reaction will not change greatly with substitution so that changes of free energy, which are related to changes of equilibrium constant ($-\Delta G = RT \ln K$), will depend mainly on changes of enthalpy of reaction which, in turn, depend on the donor power of the chelating atoms



(9) L P HAMMETT, *Physical Organic Chemistry*, p 204 McGraw-Hill, New York (1940)

The complexes formed here are considered to be chelates involving oxygen donor atoms by reason of the analogy with other diketo compounds and by virtue of the uniform relation between complex formation and acid dissociation, the latter would not be expected if the mode of complex formation varied due to substitutuents in the ring The tetrahedral arrangement of four bonds around the beryllium atom in this case should give rise to optical activity due to asymmetry of the complex molecule This could not be resolved by the usual method of diastereoisomer salt formation because the complex in neutral, it may be possible to use the NH group as a base or, in the case of the pyridine derivative, to use the heterocyclic nitrogen

It is intended to carry out infra-red work on the chelating agents and their metal complexes to indicate the method of chelation by observation of C—H and N—H frequencies and frequency shifts Dipole work is planned in connection with the conformation of the chelating agent By comparison between measured dipole moment and that calculated for the various possible structures, it should be possible to assign the correct conformation to the molecule as was done, for example, in the case of thioacetoacetic ester where six structures were possible (10) Work is at present in hand to extend these studies to other metal ions and the results will be reported later

---

(10) C F Ferraro, J J Draney and M Cefola, *J Amer Chem Soc* 75, 1206 (1953)

J Inorg Nucl Chem , 1963 Vol 25, pp 525 to 534 Pergamon Press Ltd Printed in Northern Ireland

FORMATION AND DISSOCIATION OF COPPER (II) NITROSYL COMPLEXES IN NON-AQUEOUS SOLVENTS

M Mercer* and R T M Fraser
The University of Ottawa, Ottawa, Canada and The Department of Chemistry
The University of Kansas, Lawrence, Kansas

(*Received* 22 *August* 1962)

Abstract—Solid copper nitrosyls have been isolated from alcoholic solutions, and it is found that the more stable form of these is identical with that prepared from the corresponding copper (I) and nitrosyl halides Nitrosyls containing iodide, cyanide or thiocyanate groups have been obtained in solution A new method for the evaluation of the dissociation constant of the chloride nitrosyl in alcohols has been developed the results support values obtained previously

Recent work[1] has shown that copper (II) chloride or bromide dissolved in alcohols will combine with a maximum of one equivalent of nitric oxide to form blue complexes of the composition $CuX_2 NO$(X Cl, Br or F), possibly with one or more solvent molecules coordinated to the copper These blue nitrosyls dissociate into colourless ions initially CuX_2 and NO^+ (1) these, not CuX_4^{2-}, give rise to the colour movement in ion migration experiments (2) Evidence(3) indicates that the reactions can be satisfactorily described by the equations

$$CuBr_2 + NO \longrightarrow CuBr_2\,NO$$
$$CuBr_2NO \underset{K_c}{\rightleftharpoons} CuBr_2 + NO^+$$

for the bromide and

$$CuCl_2 + NO \overset{K_f}{\rightleftharpoons} CuCl_2\,NO$$
$$CuCl_2NO \underset{K_c}{\rightleftharpoons} CuCl_2^- + NO^+$$

for the chloride (where the volume of nitric oxide absorbed is always less than one equivalent)

Values for K_c and K_f have previously been determined by measurement of the volume of nitric oxide absorbed, the concentration of the covalent nitrosyl $CuCl_2\,NO$ and (by difference) the concentration of unreacted copper (II) chloride This paper presents a method for establishing the validity of the equations and determining K_f from a knowledge only of the initial copper (II) chloride concentration and the volume of nitric oxide absorbed

Copper (I) chloride or bromide will react with the corresponding nitrosyl halide to yield a violet powder which dissolves in alcohols giving a product apparently identical to that prepared from the copper (II) halide and nitric oxide In the past it has not been possible to reverse the procedure and obtain a solid copper nitrosyl from solution the only report in the literature(4) stated that blue drops were precipitated by toluene, but these decomposed before analysis re-investigation showed that this product does not contain copper, however it is possible to precipitate a solid nitrosyl from solution the method is presented below

---

* Taken in part from the M Sc thesis of M Mercer

R T M Fraser and W E Dasent, *J Amer Chem Soc* **82**, 348 (1960)

A Kohlschutter and M Kutscheroff, *Ber Dtsch Chem Ges* **37**, 3044 (1904)

R T M Fraser, *J Inorg Nucl Chem* **17**, 265 (1961)

W Manchot, *Liebigs Ann* **375**, 308 (1910)

Information obtained from studies made of the dissociation of the nitrosyls in the series of alcohols methanol, ethanol, 1-propanol, (3) has made possible the preparation of nitrosyls of copper (II) cyanide, iodide and thiocyanate previous attempts to form these failed (5)

EXPERIMENTAL

The gas handling apparatus and the cell used for the optical measurements have been described previously (1 3) Fig 1 shows the system used for the isolation of the solid nitrosyl a saturated solution of copper (II) bromide in 10 per cent methanol 90 per cent carbon tetrachloride was prepared

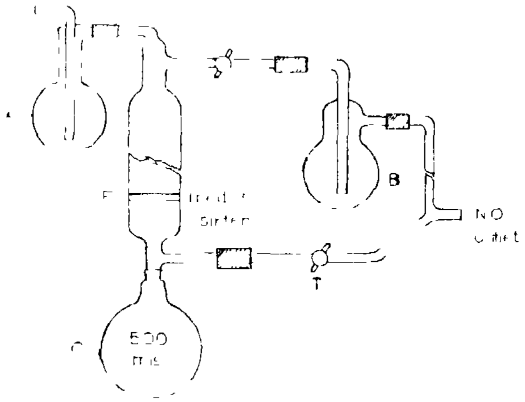


FIG 1 —Apparatus for isolation of solid nitrosyls

in the flask A and nitric oxide bubbled through for 90 min The solution was transferred to the filter *F* by inverting *A*, then petroleum ether saturated with nitric oxide was added by inverting flask *B* *F* was chilled with a freezing mixture and the nitrosyl separated as a black solid Taps S and T served to regulate the flow of nitric oxide and the rate of filtering the solution The precipitate was washed with petroleum ether or cyclohexane and dried as thoroughly as possible with a stream of nitric oxide Anhydrous copper (II) bromide and chloride the method for the preparation of these has been described (1)

Salicylal-*o*-hydroxybenzylamine copper (II) was prepared by the method of KISHITA (6) Copper (II) salicylaldoximate and copper (II) pyridine thiocyanate were prepared by standard methods (7)

The alcohols used as solvents were first refluxed with silver oxide to remove aldehydes then shaken with Drierite for 24 hr The alcohol was distilled into the volumetric flasks immediately before use Estimation of the water content of the distillate was made by titration with Karl Fischer Reagent All other solvents were dried and distilled before use

Standard methods(7) were used for the copper analyses Methanol in the complexes was determined by chromotropic acid (8)

New halide and pseudohalide nitrosyls

It seemed likely that nitrosyls of unstable copper compounds such as the cyanide and iodide would be most easily formed in alcohols such as 1-butanol or 1-propanol(3) or in methyl acetate rather than in methanol or ethanol The same procedure was used in all cases suspensions of copper (II) sulphate and the potassium salt (iodide, cyanide, thiocyanate) were prepared separately then cooled to 0 C and filtered The two solutions were mixed and nitric oxide bubbled through Optical spectra were recorded immediately in the region 400–800 mμ using a Beckman DK2 spectrophotometer

---

(5) W MANCHOT, *Ber Dtsch Chem Ges* **47**, 1601 (1914)

(6) M KISHITA, Y MUTO and M KUBO, *J Austr Chem* **12**, 386 (1957)

(7) A I VOGEL, *Quantitative Inorganic Analysis* p 432 Longmans, Green, London (1951)

(8) R N BOOS, *Analyt Chem* **20**, 964 (1948)

Treatment of data

The stability constants determined in earlier work[3] for the copper (II) chloride nitrosyl have depended on the assumption that the reactions may be adequately described by

$$\underset{c(1-x)[\mathrm{NO}]}{\mathrm{CuCl_2 + NO}} \overset{K_f}{\rightleftharpoons} \underset{cx(1-\alpha)}{\mathrm{CuCl_2\,NO}} \tag{1}$$

and

$$\underset{cx(1-\alpha)}{\mathrm{CuCl_2\,NO}} \overset{K_i}{\rightleftharpoons} \underset{cx\alpha}{\mathrm{CuCl_2^-}} + \underset{cx\alpha}{\mathrm{NO^+}} \tag{2}$$

where c is the initial concentration of copper (II) chloride, x the number of equivalents of nitric oxide absorbed per mole of copper salt ($0 < x < 1$) and α the degree of ionization of the nitrosyl If this is so

then
$$K_f = \frac{(1-\alpha)x}{\mathrm{NO}(1-x)}$$

and
$$K_i = \frac{\alpha^2 xc}{(1-\alpha)}$$

or
$$c = \frac{K_i K_f [\mathrm{NO}](1-x)}{\{x - K_f[\mathrm{NO}](1-x)\}^2}$$

For any solvent at a fixed temperature, [NO] is constant, and so if K_f and K_i can be derived from equations (1) and (2) it is possible to predict the variation in x, the uptake of nitric oxide as the initial concentration c of copper (II) chloride is decreased x will have both an upper and a lower limit, for when c is very large, $x - K_f[\mathrm{NO}](1-x)$ will tend to zero and x approach $K_f[\mathrm{NO}]/(1 + K_f[\mathrm{NO}])$ as c decreases the value of x should increase and approach 1 At high initial concentrations of copper (II) salt, the apparent volume of nitric oxide absorbed decreases this is due to the decrease of the solubility of the gas in the solution If because of this, the lower limit of x cannot be established with precision, then the value of $K_f[\mathrm{NO}]$ and hence K_f may be obtained from the slope of the central straight portion of the plot of $\log_{10} c - \log_{10} K_i K_f[\mathrm{NO}]$ against x Figure 2 shows some curves obtained for arbitrary values of $K_f[\mathrm{NO}]$ and the slopes of the mid-portions ($d \log c/dx$) are plotted against $K_f[\mathrm{NO}]$ in Fig 3 Once K_f is known, K_i may be evaluated

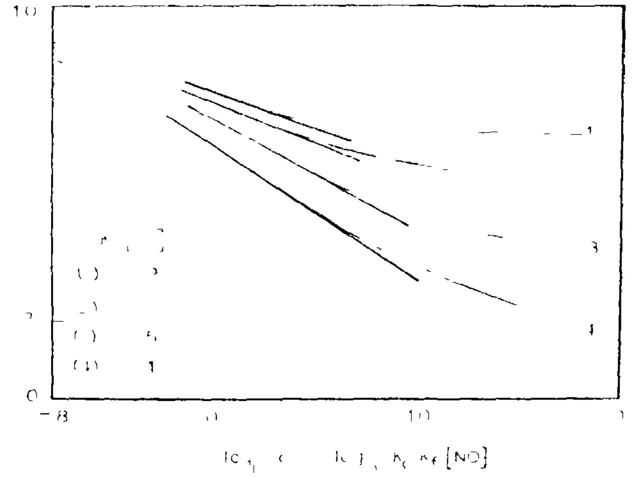


Fig. 2 – Calculated variation of nitric oxide absorption with copper (II) concentration, with slopes ($1/(dx/d \log_{10} c)$) marked

If the interaction of the nitrosonium ion with the solvent is important, a similar expression for the relationship between K_f and c and x can still be derived

$$c = \frac{8K_c K_f \mathrm{NO} K_s[\mathrm{ROH}](1 - x)}{\{x + K_f[\mathrm{NO}](1 - x)\}^2}$$

where K_s and [ROH] refer to the equilibrium

$$\mathrm{NO^+} + \mathrm{ROH} \xrightleftharpoons{K_s} \mathrm{RONO} + \mathrm{H^+}$$

The plot of x against c will again have the upper limit of 1 and the lower limit of

$$x = \frac{K_f[\mathrm{NO}]}{1 + K_f[\mathrm{NO}]}$$

but the slopes ($d \log_{10} c/dx$) will be different (Fig 3) further it is not possible to derive a value for K_c from x, c and K_f

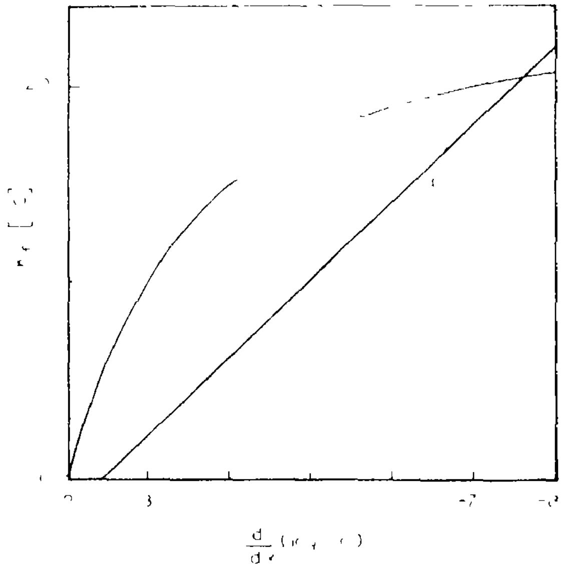


FIG 3 – Relation between K_f[NO] and the slopes ($d \log_{10} c/dx$), considering (a) two equilibria, (b) three equilibria, as the description of the systems

RESULTS

Absorption by copper (II) chloride in ethanol and methanol

Figure 4 shows the variation in the volume of nitric oxide absorbed as the concentration of the chloride was decreased A similar plot is shown (Fig 5) for copper (II) chloride in methanol Above $[\mathrm{CuCl_2}]^2$ 0 02 F the volume of nitric oxide absorbed per mole of copper did not change significantly, as shown in Table 1 Below 0 02 F the volume of nitric oxide absorbed by the copper chloride becomes very small compared with that absorbed by the solvent It was possible, however, even at the lowest copper concentrations used to detect the violet colour of the nitrosyl

New nitrosyls

(a) *Iodide, cyanide and thiocyanate nitrosyls* The iodide nitrosyl was unstable in most alcohols only in 1-propanol did a transient violet colour appear Acetone or

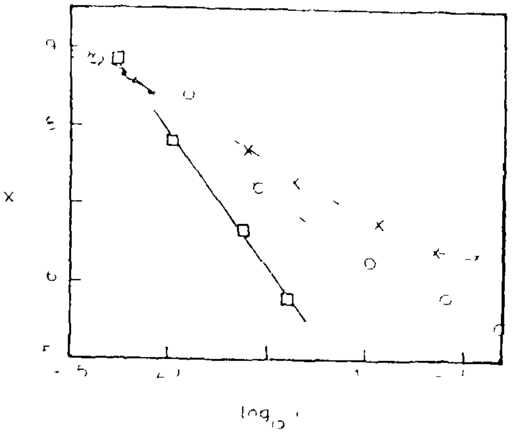


FIG 4 Experimental variation of nitric oxide absorption with copper (II) chloride concentration in ethanol (30 C, 26 2 , 16 3)

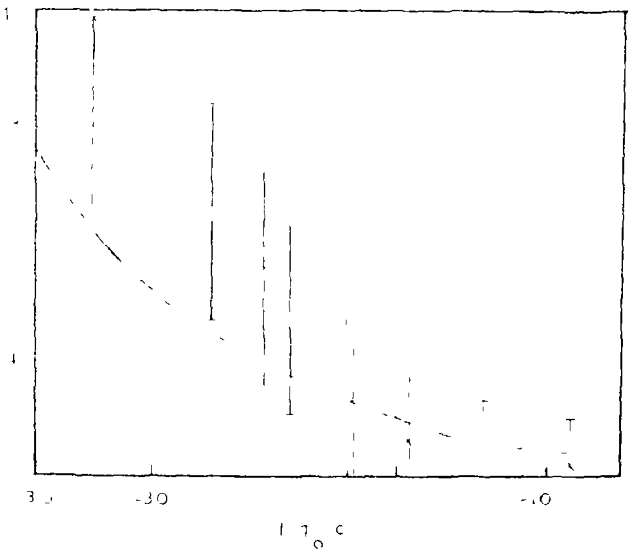


FIG 5 -Experimental variation of nitric oxide absorption with copper (II) chloride concentration in methanol (25 C) vertical lines indicate experimental error Solid curve calculated variation with K_f[NO] 0 25, $\log_{10} K_c K_f$[NO] = 2 3

TABLE I — ABSORPTION OF NITRIC OXIDE BY COPPER (II) CHLORIDE IN METHANOL (25 0 05 C)

CuCl₂ (F)	NO (equivalent (x))	CuCl₂ (F)	NO (equivalent (x))
0 02	0 20	0 137	0 25
0 039	0 22	0 16	0 25
0 04	0 26	0 18	0 22
0 08	0 20	0 20	0 20
0 092	0 20	0 20	0 23
0 10	0 25	0 22	0 20
0 11	0 25	0 24	0 24
		Average	0 23

methyl acetate were better solvents the spectrum in acetone showed a peak at 560 mμ and another at 450 mμ (due to ICH$_2$ CO– CH$_3$) The nitrosyl was stabilized by hydrogen iodide(9) and it was found that as the 560 mμ peak decreased in intensity, that at 450 mμ increased simultaneously a whitish precipitate of copper (I) iodide formed Similar behaviour was found in methyl acetate, but since the decomposition was not quite as rapid it was possible to obtain a differential spectrum against iodide The spectra are shown in Fig 6

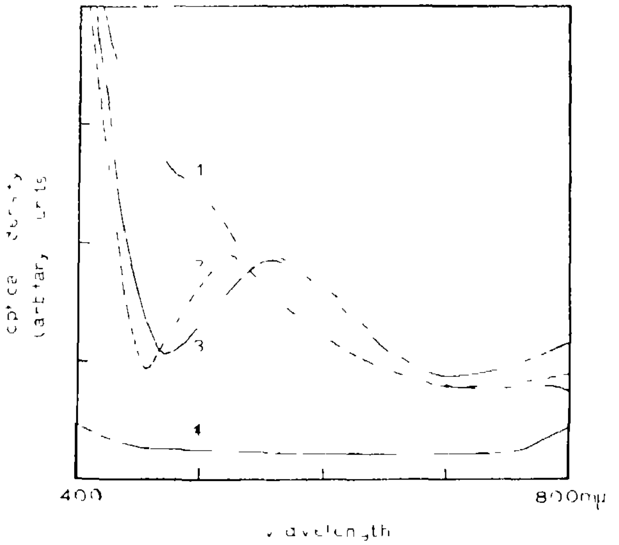


FIG 6 – Optical spectrum of the copper iodide nitrosyl 1, CuI$_2$ NO HI 2, CuCl$_2$ NO, 3, CuI$_2$ NO HI against I$_2$, 4 methyl acetate solvent blank

The thiocyanate and cyanide nitrosyls were much less stable than the iodide The The spectra obtained are shown in Fig 7 again the absorption of the decomposition products interfered Solvents used were 10% methanol in carbon tetrachloride and methyl acetate

(b) *Salicylal-o-hydroxylamine copper* (II) *nitrosyl* The dark green copper (II) salicylal-*o*-hydroxylamine dissolved readily in nonpolar solvents such as carbon tetrachloride but nitrosyl formation did not occur even after nitric oxide had been bubbled through the solution for an hour A solution of the complex (10^{-3} M) in 10 per cent methanol/90 per cent carbon tetrachloride was made, and this took up nitric oxide to become colourless and then violet, with an absorption maximum at 535 mμ

A mole ratio study was made of the chelate alone in carbon tetrachloride Methanol was added and breaks were observed in the optical density plot at 1, 2 and 3 equivalents of alcohol The experiments were repeated in the presence of nitric oxide and at the wavelength 535 mμ The optical density of the solution increased to a maximum at CH_3OH chelate — 1, then decreased as more alcohol was added When any of the nitrosyl solutions were left for several days, the violet colour deepened and a brown precipitate (which did not contain nitric oxide) formed The chelate did not form the nitrosyl in the presence of pyridine or in triethyl phosphate

---

(9) R T M FRASER, *Nature, Lond* **188**, 738 (1960)

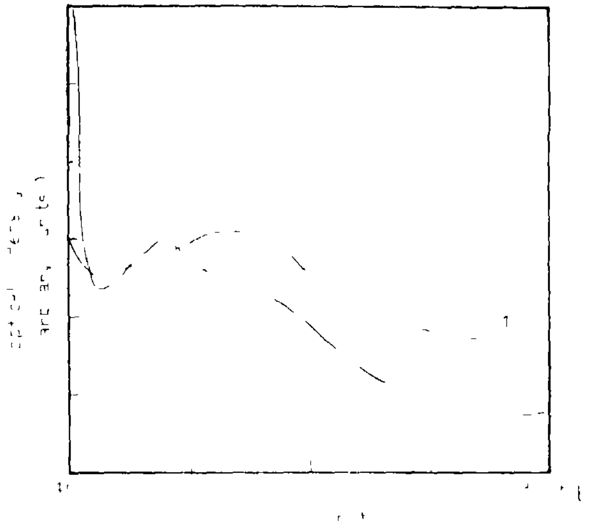


Fig. 7.—Optical spectra in methyl acetate. 1, $Cu(CN)_2NO$; 2, $Cu(SCN)_2NO$.

Preparation of solid nitrosyls

MANCHOT reported[4] that addition of toluene to the solution of a copper nitrosyl caused precipitation of pale blue crystals, but these were too unstable to examine. In this work, a solution of the copper chloride nitrosyl in ethanol was cooled in liquid air and toluene added. No precipitate formed. However, toluene and nitric oxide in the presence of traces of air will form pale blue crystals when cooled and these decompose immediately on filtering.

TABLE 2.—COPPER AND METHANOL CONTENT OF SOLID NITROSYLS

Halide	Copper (mmole)	Methanol (mmole)	Ratio MeOH/Cu
$CuCl_2$	0.197	0.186	0.94
	1.98	2.65	1.29
	50.07	48.71	0.97
$CuBr_2$	0.408	0.372	0.91
	4.01	5.82	1.45
	19.87	23.22	1.17

Isolation of the solid nitrosyls has been accomplished by a method similar to that of NAST.[10] *When the toluene was added the nitrosyl precipitated as a black powder.* This powder was washed with petroleum ether, then dried by a fast stream of nitric oxide for 40 min. Immediately after washing, the ratio of methanol to copper was 1:1, after drying with nitric oxide the nitrosyl contained no methanol but had the composition $CuCl_2NO$ or $CuBr_2NO$. Results are shown in Table 2 for the copper and methanol content found immediately after washing.

DISCUSSION

The new method for determining K_c and K_f requires only a knowledge of the volume of gas absorbed at each copper chloride concentration. It is therefore more rapid than the earlier method which involved optical and gas absorption measurements on the same sample. Further, any uncertainty in the values of the extinction coefficients cannot affect the result. In cases where x is high (between 0.6 and 0.9), the volume of gas absorbed can be measured with some precision, so that although the lower limiting value of x cannot be fixed exactly due to depression of nitric oxide solubility in concentrated solutions, the slope $d \log c/dx$ will give value for $K_f[\mathrm{NO}]$ and hence K_f then K_c. When x is low, the volume of gas absorbed is very small, but the limiting value is reached at low copper chloride concentrations, before the solubility of nitric oxide in the solvent changes significantly. The limiting value ($K_f[\mathrm{NO}]/(1 + K_f[\mathrm{NO}])$) will give K_f and then K_c may be determined by difference. In a number of cases both the slope and the limiting value can be used to determine K. Table 2 shows a comparison of K_f and K_c values with those obtained previously.

---

[10] R. NAST and H. RUCKEMANN, *Z. Anorg. Chem.* 307, 309 (1960).

That the set of two equations is adequate in describing the system is shown in Table 3, where the observed slope and those calculated from the limiting value assuming (a) two equilibria, (b) three equilibria, important are compared.

TABLE 3.—VALUES OF K_f AND K_c

Solvent	Temp	K_f	$K_f^{(1)}$	K_c	$K_c^{(1)}$
Methanol	20		5.8		1.55 10^{-2}
	25	15.6	8.2	1.7 10^{-2}	2.9 10^{-2}
	29.6		10.6		5.4 10^{-2}
	16.3	1.13 10^{2}		3.8 10^{-3}	
Ethanol	22.2		1.28 10^{2}		6.1 10^{-1}
	26.2	1.0 10^{2}	1.07 10^{2}	1.35 10^{-2}	1.4 10^{-}
	30.0	5 10			

TABLE 4.—OBSERVED AND CALCULATED SLOPES ($d \log c/dx$)

ETHANOL AS SOLVENT

Temp	x (Limit)	Obs	Slope calcd (a)	Calcd (b)
16.3	0.63	6.6	6.7	−5.2
22.2	0.57	−5.0	5.7	−3.8
30.0	0.38	−2.8	3.9	2.6

As the temperature increases, the reaction of the dissociation products with the solvent may be expected to become more important and the three equilibria describe the system better. Thus in ethanol at 30°, the slope found is closer to the calculated (b) value.

Traces of water in the methanol depress the volume of gas absorbed by the copper chloride and it was found necessary to use Drierite rather than magnesium turnings(1) to dry the solvent. Titration with Karl Fischer Reagent showed that this treatment reduced the water content below 0.002 per cent. The effect of water was first stressed by MANCHOT(4) in his studies of copper chloride in ethanol, and in fact, if the data for nitric oxide absorption contained in that paper are plotted against concentration, a variation is found similar to that shown in Fig. 4; the values of x are a little low since the hydrated copper salt was used.

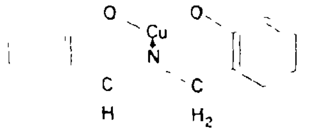
The four halide nitrosyls have now been prepared in solution. The copper bromide and chloride nitrosyls are the most stable, and form in any alcohol, ketone and in some nitriles. Copper (II) fluoride will react with nitric oxide in 1-butanol to give a very short-lived violet complex,(9) which can be stabilized by hydrogen fluoride. In the presence of this acid, even ethanol or propanol will serve as a satisfactory solvent. A similar method has been used to stabilize the iodide nitrosyl in acetone, methyl acetate and 1-propanol, but even in the presence of acid the lifetime of this complex is less than thirty seconds. As the precipitate of copper (I) iodide forms, an equivalent amount of iodine is liberated; this, together with the similarity of the optical spectrum with that of the chloride nitrosyl, seems good evidence for the composition CuI_2NO.

Very dilute solutions of copper (II) sulphate and potassium cyanide or thiocyanate behave in the same way; the violet complex is even more unstable, decomposing in less than twenty seconds. Copper (II) hydroxide, nitrate (and of course sulphate) do not form nitrosyls in alcohols or methyl acetate.

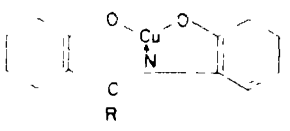
In contrast to these compounds, copper (II) salicylal-*o*-hydroxybenzylamine is most soluble in non-polar liquids such as benzene or carbon tetrachloride. It is possible therefore to observe the effects of added trace amounts of alcohols, and since these are necessary for the formation of a nitrosyl, to carry out a mole ratio study. In the presence of nitric oxide, the chelate forms a nitrosyl containing one alcohol molecule. The light absorption maximum occurs at 535 mμ, but the extinction coefficient is very small (approx. 100) compared to that of the copper chloride nitrosyl. When more than one equivalent of alcohol is added to the solution and nitric oxide passed in, the nitrosyl color appears in about thirty minutes. Over a period of three days the purple colour deepens and a known precipitate forms. The precipitate is not a nitrosyl, but does contain some copper. If the solution is treated with nitrogen and then evaporated, it does not yield the starting material but some decomposition products.

The mole ratio experiments seem to indicate that the salicylal nitrosyl is five-co-ordinate; this is probably the coordination number of the halide nitrosyls as well with two solvent molecules completing the shell. There is no evidence for a further solvent molecule in the complex; if the nitrosyls are six-covalent, the last alcohol must be bound very loosely.

Copper (II) bromide or chloride form a very stable nitrosyl in triethyl phosphate, whereas copper (II) salicylal-*o*-hydroxylamine does not form one at all. Of the six possible co-ordination positions about the copper, only two are required (by the halogen atoms) for the halide nitrosyls. The nitric oxide and the solvent molecules may occupy any of the other positions, all of which are unhindered. A study of molecular models shows that the monomer of copper (II) salicylal-*o*-hydroxylamine (I) is non-planer, in contrast to related compounds such as II, which are planar in the solid state.(11)



I



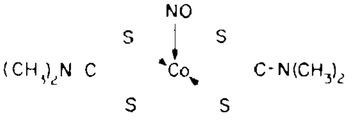
II

---

(11) A. Barclay, C. M. Harris, B. F. Hoskins and E. Kokot *Proc. Chem. Soc.* 264 (1961).

Three of the six octahedral positions about the copper are already filled of the remaining three, only one, *trans* to the nitrogen, is unhindered Methanol or ethanol can just occupy either one of the remaining two vacancies, but triethyl phosphate is too large a co-ordinating group to fit anywhere but trans to the nitrogen Apparently, if this position is filled, nitric oxide will not occupy either of the other two, and so no nitrosyl is obtained

It has been found(12) that the position of the infra-red absorption of the nitrogen–oxygen (NO) group in the complexes is related to the type of metal–nitrogen bonding while nitric oxide absorbs at 1878 cm^{-1} and the nitrosonium ion at 2220 cm^{-1}, the metal nitrosyls containing the NO^{+} group absorb in the region 1938 cm^{-1} ([NOFe(CN)$_5$]$^{2-}$) to 1626 cm^{-1} (NOCo[(CH$_3$)$_2$NCS$_2$]) The spread in values may be attributed to different multiple metal nitrogen bonding the more backbonding, the higher the frequency Copper (II) chloride and bromide nitrosyls show absorptions at 1854 and 1848 cm^{-1} respectively, while the copper (II) salicylal nitrosyl absorbs at 1640 cm^{-1} After decomposition, this value rises to around 1780 cm^{-1} The low value of 1640 may arise from the same cause as that of 1626 cm^{-1} found for NOCo[(CH$_3$)$_2$NCS$_2$]$_2$, where asymmetric coordination of the nitric oxide (III) has been proposed,(13) but without supporting evidence



III

The blue crystals that Manchot reported as the solid nitrosyl are merely a mixture of toluene and nitric oxide They decompose immediately on exposure to air, and this is why he was unable to examine them If an alcoholic solution of the nitrosyl is treated with excess petroleum ether and cooled in a dry-ice–acetone or liquid nitrogen bath, it is possible to obtain a black precipitate which contains copper (chlorine or bromine depending on the copper halide) nitric oxide and some alcohol about one equivalent per copper The amount found varied somewhat, the highest value being about 3 2 It was not possible to establish whether the variation was due to incomplete washing or whether more than one solvated nitrosyl was present The alcohol is lost quite readily and the stable nitrosyl is identical with that prepared from copper (I) chloride or bromide and the corresponding nitrosyl halide

---

(12) W P Griffith, J Lewis and G Wilkinson, *J Chem Soc* 3993 (1958)

(13) J Lewis, R J Irving and G Wilkinson, *J Inorg Nucl Chem* 7, 32 (1958)

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 535 to 544. Pergamon Press Ltd. Printed in Northern Ireland

THE THERMAL DISSOCIATION OF POTASSIUM METHYL- AND ETHYLSULPHATES. THERMOGRAVIMETRIC ANALYSIS, DIFFERENTIAL THERMAL ANALYSIS, GAS EVOLUTION AND X-RAY STUDIES

W. W. WENDLANDT and E. STURM
Departments of Chemistry and Geosciences, Texas Technological College
Lubbock, Texas

(*Received* 13 *August* 1962)

Abstract—The thermal dissociation of potassium methyl- and ethylsulphates was studied by thermogravimetric analysis, differential thermal analysis, gas evolution analysis, and by X-ray diffraction. Two new phase transitions were found: $\alpha \rightarrow \beta$ KCH_3SO_4 at ~110°C, and $\alpha \rightarrow \beta$ $KC_2H_5SO_4$ at ~87°C. The heats of transition for the two transitions were 1,800 and 2,000 cal mole^{-1}, respectively. The dissociation reactions found were as follows: $KCH_3SO_4 \rightarrow K_2S_2O_7 + (CH_3)_2O \rightarrow K_2SO_4 + SO_3$, and $KC_2H_5SO_4 \rightarrow K_2S_2O_7 + C_2H_4 + H_2O \rightarrow K_2SO_4 + SO_3$. X-ray diffraction data are given for all of the solid phases involved in the reactions.

IN connection with his studies on the thermal dissociation of the rare-earth ethylsulphate hydrates, NATHANS$^{(1)}$ studied the thermal dissociation of potassium ethylsulphate. The differential thermal analysis (DTA) curve consisted of a single endothermic peak with a peak maxima temperature of 200°C. On the basis of this curve and an analysis of the residue, he stated that the compound dissociated according to the reaction

$$KC_2H_5SO_4(s) \rightarrow KHSO_4(s) + C_2H_4(g) \qquad (1)$$

As a result of studies in this Laboratory, it was found that NATHANS had used a partially decomposed sample of potassium ethylsulphate.$^{(2)}$ Consequently, this study is concerned with the investigation of the thermal dissociation of potassium ethylsulphate and of potassium methylsulphate by the methods of thermogravimetric analysis (TGA), DTA, gas evolution analysis (GE) and X-ray diffraction.

EXPERIMENTAL

Chemicals. Potassium ethylsulphate (ethylsulphuric acid potassium salt No. 916) was obtained from Eastman Organic Chemicals, Rochester, N.Y. Analysis of the compound gave: carbon, 14.31% found, 14.62% theor.; hydrogen, 2.85% found, 3.05% theor. Previous thermal history included drying in a hot-air oven at 60°C for 48 hr.$^{(3)}$

Potassium methylsulphate, electronic grade, was obtained from City Chemical Corp., New York, N.Y. Analysis of the compound gave: carbon, 7.88% found, 7.99% theor.; hydrogen, 2.02% found, 2.01% theor. Previous thermal history included being air dried at 70°F for several hours.$^{(4)}$

Thermobalance. The automatic recording thermobalance has previously been described.$^{(5)}$ Samples weighed about 60 mg and were pyrolysed in an air atmosphere at a heating rate of about 5°C per minute.

Differential thermal analysis and gas evolution apparatus. The DTA–GE apparatus has previously

---

M. W. NATHANS, *J. Inorg. Nucl. Chem.* **22**, 231 (1961).

M. W. NATHANS, Private communications. Analysis of compound: carbon, 6.63%; hydrogen, 1.78%.

R. C. HAPEMAN, Private communication.

I. R. KELLER, Private communication.

W. W. WENDLANDT, T. D. GEORGE and G. R. HORTON, *J. Inorg. Nucl. Chem.* **17**, 273 (1961).

been described [6] Sample sizes ranged in weight from 40 to 50 mg and were pyrolysed in a dynamic helium gas atmosphere at a heating rate of about 10 per min Ignited alumina was used as the reference material

Quantitative DTA studies The general procedure was the same as that previously described[7] except that the sample and reference compounds were contained in small Inconel cups Sample sizes ranged in weight from 75 to 80 mg The curve endothermic peaks were integrated by means of an attached Sargent Model SR strip-chart recorder equipped with a Disc Model 204 integrator The system was calibrated with $BaCl_2 2H_2O$, ΔH 26 83 kcal mole $^{-1}$, giving a calibration constant of 0 004121 cal per integrator count

X-ray apparatus X-ray diffraction patterns were taken on a Norelco diffractometer manufactured by Philips Electronics Inc using Ni-filtered Cu $K\alpha$ radiation at 30 kV and 15 mA

Gas analysis The evolved gases from the thermal dissociation of the compounds were analyzed by a Consolidated Engineering Co Model 21-620 mass spectrometer, a Perkin-Elmer Model 154-D gas chromatograph and a Perkin-Elmer Model 237 spectrophotometer

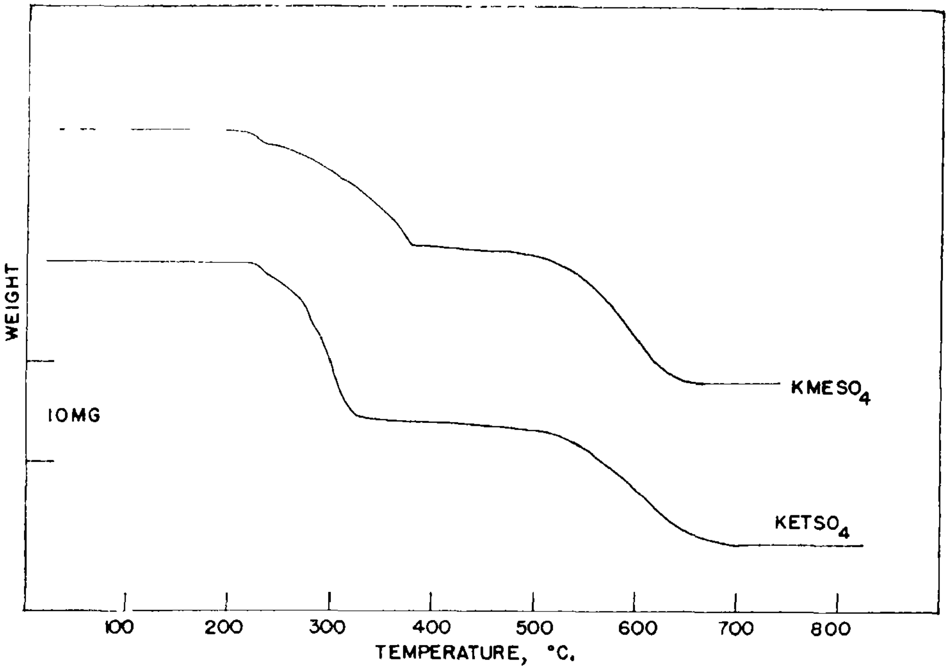


FIG 1 Weight-loss curves for potassium methyl- and ethylsulphates

RESULTS AND DISCUSSION

TGA studies The weight-loss curves are given in Fig 1 while the percentage weight-loss data are given in Table 1

From the weight-loss curves and the corresponding weight data, it is seen that both of the compounds gave an intermediate compound with the composition, $K_2S_2O_7$ However, the decomposition mechanism was not the same for both compounds

The decomposition reactions observed were as follows

For $KC_2H_5SO_4$

$$KC_2H_5SO_4(s) \xrightarrow{220\text{–}340\ ^\circ C} K_2S_2O_7(s) + C_2H_4(g) + H_2O(v) \qquad (2)$$

$$K_2S_2O_7(s) \xrightarrow{470\text{–}700\ ^\circ C} K_2SO_4(s) + SO_3(g) \qquad (3)$$

---

(6) W W WENDLANDT, *Anal Chim Acta* **27**, 309 (1962)

(7) W W WENDLANDT and T D GEORGE, *J Inorg Nucl Chem* **19**, 245 (1961)

TABLE I.—WEIGHT-LOSS DATA FOR POTASSIUM METHYL- AND ETHYLSULPHATES

Compound	Weight-loss (%)	
	$K_2S_2O_7$	K_2SO_4
	400 C	740 C
KCH_3SO_4	21.34, theor	41.99, theor
(60.84 mg)	19.2, found	41.9, found
$KC_2H_5SO_4$	400 C	800 C
(60.76 mg)	26.44 theor	46.94 theor
	26.3, found	47.1, found

For KCH_3SO_4

$$KCH_3SO_4(s) \xrightarrow{210-390 °C} K_2S_2O_7(s) + (CH_3)_2O(g) \quad (4)$$

$$K_2S_2O_7(s) \xrightarrow{450-700 °C} K_2SO_4(s) + SO_3(g) \quad (5)$$

The presence of $K_2S_2O_7$ as an intermediate compound, not $KHSO_4$ (4) is definitely indicated. This was later confirmed by X-ray data on the 400°C residues. Perhaps the mechanism for the thermal dissociation of $KC_2H_5SO_4$ involves the formation of $KHSO_4$ which then splits off water as shown in Equation (2). However, the formation of a stable intermediate compound with the composition of $KHSO_4$ is not indicated under the conditions of these experiments.

DTA and GE studies. The DTA and GE curves are given in Figs. 2–4.

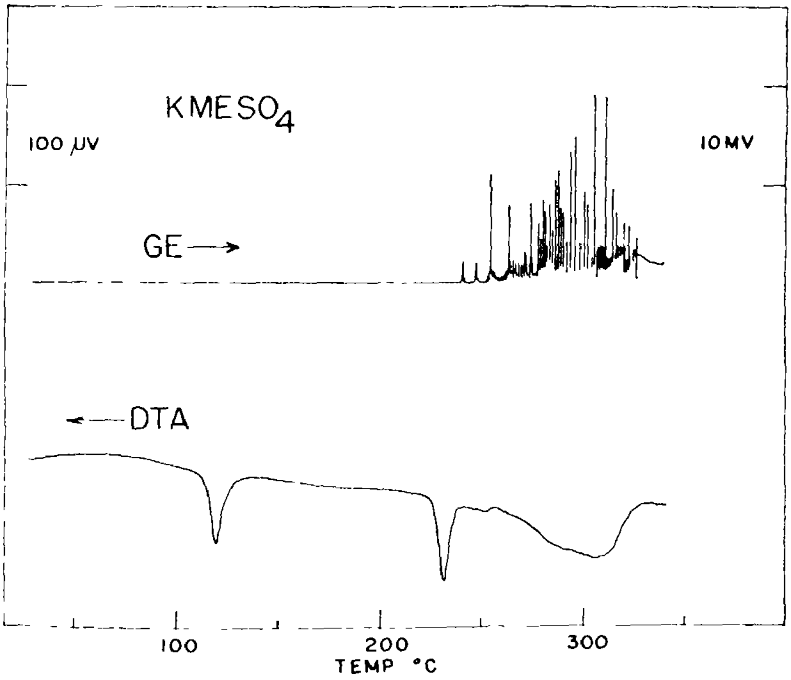


FIG. 2.—DTA and GE curves for potassium methylsulphate.

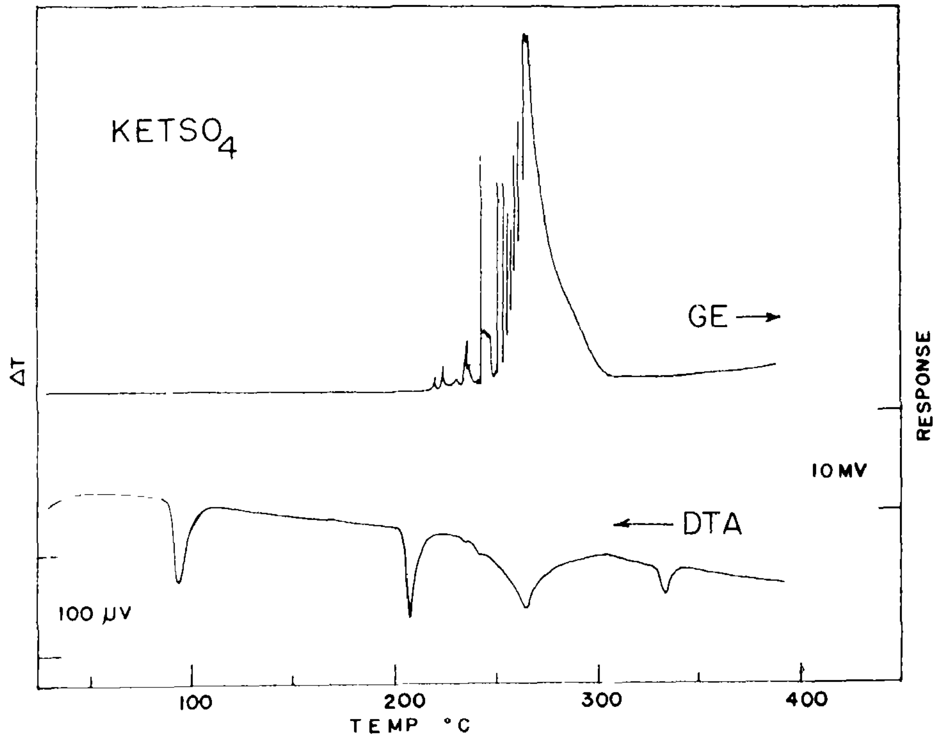


FIG. 3 DTA and GE curves for potassium ethylsulphate

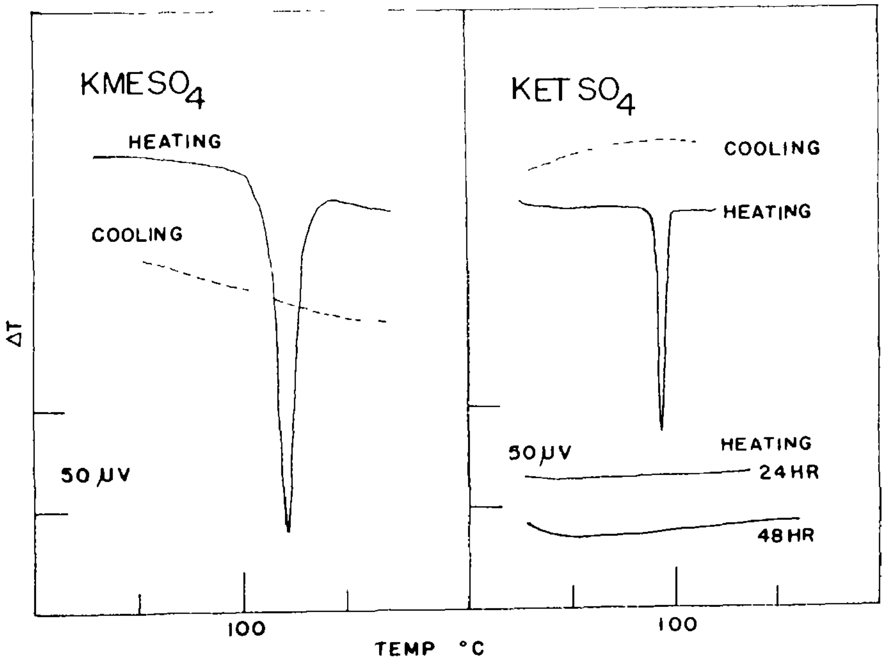


FIG. 4 The irreversibility of the $\gamma \rightarrow \beta$ phase transition of potassium methyl- and ethylsulphates

A rather unexpected development was discovered in the DTA curves in that two new crystalline phase transitions were detected. The phase transition for $KC_2H_5SO_4$, as indicated by the DTA curve, began at 87°C and had a peak maximum temperature of 93°C. For KCH_3SO_4, the transition began at 110°C and had a peak maximum temperature of 120°C. These transitions involved the following solid phases:

$$\alpha - KCH_3SO_4(s) \xrightarrow{\sim 110°C} \beta - KCH_3SO_4(s)$$
$$\alpha - KC_2H_5SO_4(s) \xrightarrow{\sim 87°C} \beta - KC_2H_5SO_4(s)$$

A gaseous component was not evolved during these phase transitions, as indicated by the corresponding GE curves.

To determine whether or not the phase transition were reversible, the furnace was allowed to cool and the DTA curve of the cooling process recorded. From Fig. 4, it is seen that the transitions were not reversible and that the β-forms did not revert back to the α-forms on standing at room temperature for various periods of time.

On further heating, the DTA curves showed that the compounds fused, as indicated by the endothermic peaks with peak maxima temperatures at 207 and 233°C, for $KC_2H_5SO_4$ and KCH_3SO_4, respectively. This was in good agreement with the reported fusion temperatures of 203–204.5°C and 228–230°C, for $KC_2H_5SO_4$ and KCH_3SO_4, respectively. Both compounds did not evolve gaseous products during fusion but did so at slightly higher temperatures. The gas evolution from the compounds was not a smooth continuous process as indicated by the high speed recorder curves on the GE apparatus. Rather, it involved the evolution of gas from the liquid metal alkylsulphates and took place in short sporadic bursts. The dissociation process was indicated by broad endothermic peaks on the DTA curves. Possibly another phase transition was present in the $KC_2H_5SO_4$ curve as indicated by the small endothermic peak at 333°C, since it was not accompanied by a corresponding peak on the GE curve.

Attempts were made to study the kinetics of the dissociation process by recording the gas evolution under isothermal conditions but they were unsuccessful due perhaps to the sporadic nature of the reaction.

Heats of transition studies. The heats of transition, ΔH, for the $\alpha \rightarrow \beta$ transition of the metal alkylsulphates were determined by quantitative DTA techniques. This technique is based upon the premise that the area enclosed by the DTA peak is related to the heat of reaction, ΔH, by the relationship^(8, 9)

$$\text{peak area} = \int_{t_1}^{t_2} \Delta T \, dt = \frac{\Delta H m}{\lambda g}$$

where ΔT is the differential temperature between the sample and reference material, t_1 and t_2 are the time at the beginning and end of the reaction, m is the mass of the reactive sample, λ is the thermal conductivity of the sample, and g is the geometrical shape constant for the apparatus. By calibration with a compound of known thermal transitions, a constant, k, is obtained, so that

$$\Delta H = \frac{k}{m} \int_{t_1}^{t_2} \Delta T \, dt$$

---

(8) Speil, L. H. Berkelhamer, J. A. Pask and B. Davis, *U.S. Bur. Min. Tech. Paper* **664** (1954).

(9) S. L. Boersma, *J. Amer. Ceram. Soc.* **38**, 281 (1955).

TABLE 4. X-RAY DATA FOR α- AND β- FORMS OF KCH_3SO_4 (UNCORRECTED)

α- form		β- form	
d (Å)	I/I_0*	d (Å)	I/I_0*
9.17	1.00	9.21	1.00
5.54	0.03	5.55	0.16
5.07	0.03	5.06	0.10
4.61	0.85	4.61	0.48
4.35	0.04	4.35	0.13
3.83	0.07	3.84	0.12
3.65	0.06	3.68	0.09
3.47	0.07	3.48	0.34
3.34	0.04	3.35	0.23
3.25	0.03	3.27	0.10
3.14	0.04	3.15	0.31
3.08	0.75	3.07	0.38
0.95	0.05	2.96	0.22
2.78	0.06	2.79	0.15
2.72	0.03	2.72	0.16
2.63	0.03	2.64	0.15
2.58	0.11	2.59	0.13
2.42	0.03	2.42	0.10
2.31	0.11	2.31	0.21
2.23	0.08	2.27	0.07
2.19	0.02	2.23	0.12
2.07	0.11	2.18	0.10
1.76	0.03	2.08	0.15
1.68	0.02	1.98	0.12
1.64	0.02		
1.54	0.03		
1.50	0.02		
1.49	0.02		
1.46	0.03		
1.45	0.04		
1.39	0.02		
1.37	0.05		
1.30	0.02		
1.29	0.03		
1.27	0.03		
1.20	0.07		

* Peak intensities

TABLE 5.—X-RAY DATA FOR THE PRODUCT FORMED BY HEATING $KC_2H_5SO_4$ TO 400 °C (UNCORRECTED)

d (Å)	I/I_0*	*d* (Å)	I/I_0*
6.25	0.10	2.09†	0.17
4.80†	0.52	2.08	0.09
4.68	0.27	2.01†	0.08
4.14†	0.14	1.94†	0.20
3.95	0.13	1.90†	0.07
3.85†	0.14	1.89	0.06
3.65†	0.58	1.83†	0.11
3.57	0.38	1.77	0.13
3.24	1.00	1.76†	0.15
3.20	0.79	1.75	0.14
3.07†	1.00	1.72	0.21
2.99	0.30	1.69	0.11
2.90†	0.57	1.67	0.12
2.88	0.42	1.66	0.10
2.62†	0.22	1.61	0.10
2.49†	0.15	1.59	0.13
2.41	0.17	1.53	0.09
2.35†	0.24	1.44	0.13
2.27	0.24	1.43	0.14
2.20†	0.20	1.41	0.13

* Peak intensities † $K_2S_2O_7$ lines

TABLE 6.—X-RAY DATA FOR THE PRODUCT FORMED BY HEATING KCH_3SO_4 TO 400 °C (UNCORRECTED)

d (Å)	I/I_0*	*d* (Å)	I/I_0*
9.15‡	1.00	2.60†	0.22
5.56‡	0.26	2.58‡	0.22
5.05‡	0.28	4.49†	0.15
4.80†	0.25	2.41†	0.28
4.61‡	0.77	2.31‡	0.25
4.35‡	0.25	2.26†	0.22
3.83†	0.27	2.24†	0.25
3.70	0.32	2.19†	0.20
3.65†	0.36	2.07‡	0.25
3.58	0.34	2.01†	0.13
3.48‡	0.65	1.98	0.24
3.34	0.43	1.94†	0.26
3.25†	0.69	1.89†	0.07
3.15‡	0.90	1.87	0.11
3.07†‡	1.00	1.86	0.13
2.95‡	0.43	1.81	0.13
2.89†	0.34	1.72	0.13
2.79	0.32	1.68	0.13
2.78‡	0.34	1.68	0.15
2.72‡	0.27	1.67	0.15

* Peak intensities

† $K_2S_2O_7$ lines ‡ Lines due to remaining structural entities

was monoclinic also. It should be noted that α- $KC_2H_5SO_4$ is a rather unstable compound due perhaps to the reaction with water vapor to give

$$KC_2H_5SO_4 + H_2O \rightarrow KHSO_4 + C_2H_5OH$$

A sample of the γ-form gave several X-ray lines of $KHSO_4$ after standing in a capped container at room temperature for about four months.

X-ray diffraction data on the intermediate compounds formed at 400°C are given in Tables 5 and 6. The intermediate compounds consisted mainly of $K_2S_2O_7$ which is a confirmation of the data found from the weight-loss studies. A number of *d*-space values were found in the KCH_3SO_4 intermediate compound which were identical to those of the original sample. These lines were probably due to a small amount of undecomposed KCH_3SO_4.

Acknowledgements. The helpful assistance of Mr. J. HOIBERG is gratefully acknowledged. The continued interest and assistance of Dr. M. W. NATHANS is greatly appreciated.

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 545 to 551. Pergamon Press Ltd. Printed in Northern Ireland

THERMAL DECOMPOSITION OF METAL COMPLEXES—III

STOICHEIOMETRY OF THE THERMAL DISSOCIATION OF SOME HEXAMMINECOBALT (III) COMPLEXES

W. W. Wendlandt
AFOSR Center for Molecular Research, Department of Chemistry
Texas Technological College, Lubbock, Texas

(*Received* 20 *August* 1962; *in revised form* 10 *October* 1962)

Abstract—The stoicheiometry and probable decomposition sequence for the thermal dissociation of $[Co(NH_3)_6]X_3$, where X is Cl, Br, NO_3, and $[Co(NH_3)_6]_2(SO_4)_3 \cdot 2.5H_2O$, are presented. Differential thermal analysis and gas evolution curves are presented for each of the complexes. The data shows that the reduction of Co(III) → Co(II) is due to ammonia, forming NH_4X (X = Cl, Br or SO_4) and nitrogen. No free halogen could be detected. Due to the presence of both oxidizing and reducing groups $[Co(NH_3)_6](NO_3)_3$ decomposed in a different manner than the other three compounds.

Biltz[(1)] was the first to investigate the thermal dissociation of several hexamminecobalt (III) complexes. He found that $[Co(NH_3)_6]Cl_3$ decomposed in two steps. The first step, at 215°C, in an ammonia atmosphere, resulted in the formation of $[Co(NH_3)_5Cl]Cl_2$ and ammonia. In the second step, the pentammine decomposed, when heated to 250°C, to give $CoCl_2$, NH_4Cl, ammonia and nitrogen. Similarly, for $[Co(NH_3)_6]PO_4$, it was shown to decompose, at 190–200°C in a carbon dioxide atmosphere, to give $Co_2P_2O_7$, ammonia, water and nitrogen. The stoicheiometry for both thermal dissociation reactions was determined.

The above work was confirmed by Clark *et al.*[(2)] for the chloride but the decomposition temperatures were somewhat lower and also a residue of $CoCl_2 \cdot 2NH_4Cl$ was obtained. The latter resulted from thermal dissociation at 260°C under vacuum but it was stated that this composition may be fortuitous since a sublimate of NH_4Cl was also noted. Probable mechanisms for the thermal dissociation of $[Co(NH_3)_5NO_2]Cl_2$ and $[Co(NH_3)_3(NO_2)_3]$ were also presented. Both of these compounds gave Co_2O_3, nitrogen, water, ammonia and NH_4Cl (the last two for the chloride only). Only meagre quantitative data was presented, however, to substantiate the reaction stoicheiometry.

More recent work on the thermal dissociation of $[Co(NH_3)_6]Cl_3$, as studied by thermogravimetric analysis (TGA) and differential thermal analysis (DTA)[(3,4)], showed the presence of new intermediate compounds. The thermal dissociation, in an ammonia atmosphere, proceeded according to the sequence $[Co(NH_3)_6]Cl_3 \xrightarrow{240} CoCl_2 \cdot NH_3 \cdot NH_4Cl \xrightarrow{285} CoCl_2 \cdot NH_3 \xrightarrow{100} CoCl_2 \xrightarrow{150} Co$. The nature of the reduction of Co(III) → Co(II) in step one was rather obscure. Isothermal heating of the chloride at 215–220°C gave $[Co(NH_3)_5Cl]Cl_2$ although a DTA study showed that $[Co(NH_3)_{5.5}Cl_{0.5}]Cl_{2.5}$ was an intermediate in the reaction A DTA study, in an air atmosphere (4) showed that *t*-$[Co(NH_3)_4Cl_2]Cl$ was formed, this was then transformed to *c*-$[Co(NH_3)_4Cl_2]Cl$ on further heating

---

(1) W. Biltz, *Z. Anorg. Chem.* **83**, 177 (1913).

(2) C. L. Clark, A. J. Quick and W. D. Harkins, *J. Amer. Chem. Soc.* **42**, 2496 (1920).

(3) I. Kekedy, A. Szurkos, P. Krobl and L. Kekedy, *Acad. Rep. populare Romine, Filiala Cluj, Studii Cercetari Chim.* **9**, 79 (1958).

(4) I. Kekedy, A. Szurkos, E. Kekedy and P. Krobl, *Acad. Rep. populare Romine, Filiala Cluj, Studii Cercetari Chim.* **9**, 91 (1958).

Previous TGA and DTA studies on several amminecobalt (III) complexes have been made in this Laboratory[5-7] Although the minimum decomposition temperatures and thermal effects were recorded the stoichiometry as revealed by analysis of the thermal dissociation products was not determined It is thus the object of this investigation to determine the stoichiometry of the thermal dissociation reaction for several complexes of the type $[Co(NH_3)_6]X_3$ where X is Cl, Br NO_3, and $[Co(NH_3)_6]_2(SO_4)_3$

EXPERIMENTAL

Preparation of complexes The compounds $[Co(NH_3)_6]X_3$ (X = Cl, Br NO_3) were prepared according to the procedures as previously described[8] The compound $[Co(NH_3)_6]_2(SO_4)_3 \cdot 2.50H_2O$ was prepared as previously described[9] The complexes were analysed in the following manner (a) Halide by $Hg(NO_3)_2$ titration using sodium nitroprusside as indicator, (b) cobalt by ignition to cobalt halide or oxide either under nitrogen or air (c) ammonia by the Kjeldahl method, (d) water by dehydration in a helium atmosphere and collection in a tared BaO filled U tube

The results of the analyses are given below

$[Co(NH_3)_6]Cl_3$ Cl 39.79% found 39.76% calc , Co 22.06% found, 22.03% calc , NH_3 37.84% found, 38.20% calc

$[Co(NH_3)_6]Br_3$ Br, 59.47% found, 59.81% calc , Co 14.72% found, 14.70% calc NH_3 24.86%, found 25.49% calc

$[Co(NH_3)_6](NO_3)_3$ Co, 16.89% found 16.98% calc NH_3 28.45% found 29.43% calc ,

$[Co(NH_3)_6]_2(SO_4)_3 \cdot 2.5H_2O$, H_2O, 6.70% found, 6.87% calc , Co, 17.31% found, 17.98% calc NH_3 29.42% found 31.18% calc

DTA and GE studies The simultaneous DTA and gas evolution (GE) curves were determined on the apparatus previously described[10] Sample sizes ranged in weight from 40 to 50 mg and were decomposed in a helium atmosphere (flow-rate of 100 ml min^{-1}) at a heating rate of 10 ± 1°C The output voltages from the DTA d c amplifier and the thermistor bridge circuit were recorded as a function of furnace temperature on separate X-Y recorders Duplicate and triplicate samples gave resultant peak temperatures which were within ± 1 per cent of each other

Analysis of decomposition products The ammonia was determined in the following manner a sample of the compound was pyrolysed in an enclosed Vycor glass tube-furnace through which flowed a stream of helium gas at a flow-rate of 50 ml min^{-1} The evolved ammonia in the helium gas stream was collected in standard 0.06 N hydrochloric acid The excess acid, after the run, was then back-titrated with 0.06 N sodium hydroxide, using a Fisher Scientific Co Titrimeter

The water in the decomposition gases was determined as described previously

The nitrogen and other gaseous decomposition products were determined, from gas samples collected by pyrolysis of the complexes in a vacuum system, by mass spectrographic analysis using a Consolidated Engineering Corp Model 21-620 mass spectrometer The N_2 NH_3 and N_2O-NH_3 ratios were determined from standard samples containing the above gases The results obtained in the mass spectrographic analysis were probably only good to about ± 5 per cent

The amount of residue of the decomposition reactions were determined by weighing

The ammonium compounds such as NH_4Cl NH_4Br etc , were not determined quantitatively due to experimental difficulties In all cases, however these compounds were detected in a qualitative manner

---

(5) W W WENDLANDT *Tex J Sci* **10**, 271 (1958).

(6) W W WENDLANDT, T D GEORGE and K V KRISHNAMURTY, *J Inorg Nucl Chem* **21**, 69 (1961)

(7) W W WENDLANDT and J L BEAR *J Phys Chem* **65**, 1516 (1961)

(8) J BJERRUM and J P MCREYNOLDS, *Inorganic Syntheses* (Edited by W C Fernelius) Vol 2 p 217 220, McGraw-Hill New York (1946)

(9) S M JORGENSEN, *Z Anorg Chem* **17**, 458 (1898)

(10) W W WENDLANDT, *Analyt Chim Acta* **27**, 309 (1962)

RESULTS AND DISCUSSION

DTA and GE results The DTA and GE curves are given in Figs 1-4 respectively The DTA and GE curves for $[Co(NH_3)_6]Cl_3$ gave only slight evidence for the formation of the pentamine, $[Co(NH_3)_5Cl]Cl_2$, as previously reported(1 2) However, this may be due to the fairly rapid heating rate employed The compound began to decompose at about 200°C, somewhat lower than the 215 and 240°C decomposition

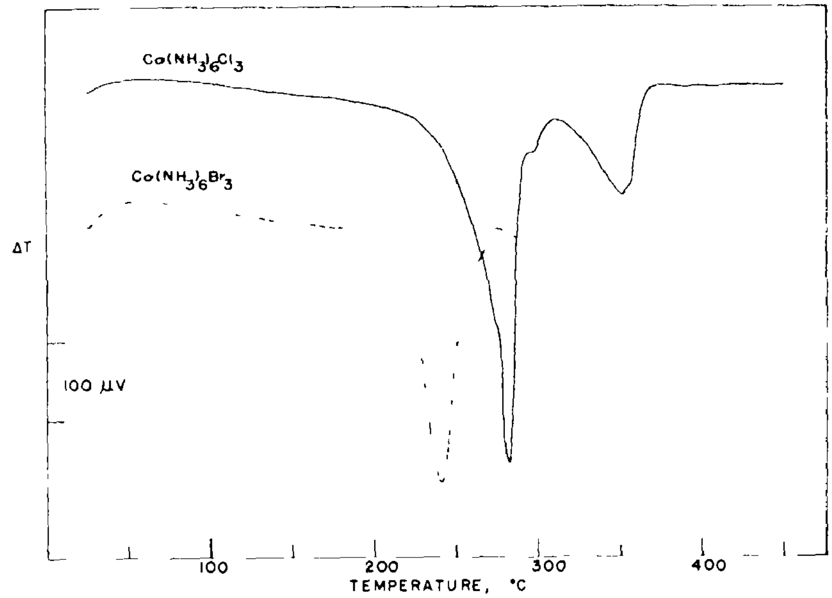


Fig. 1 Differential thermal analysis curves of hexamminecobalt (III) complexes

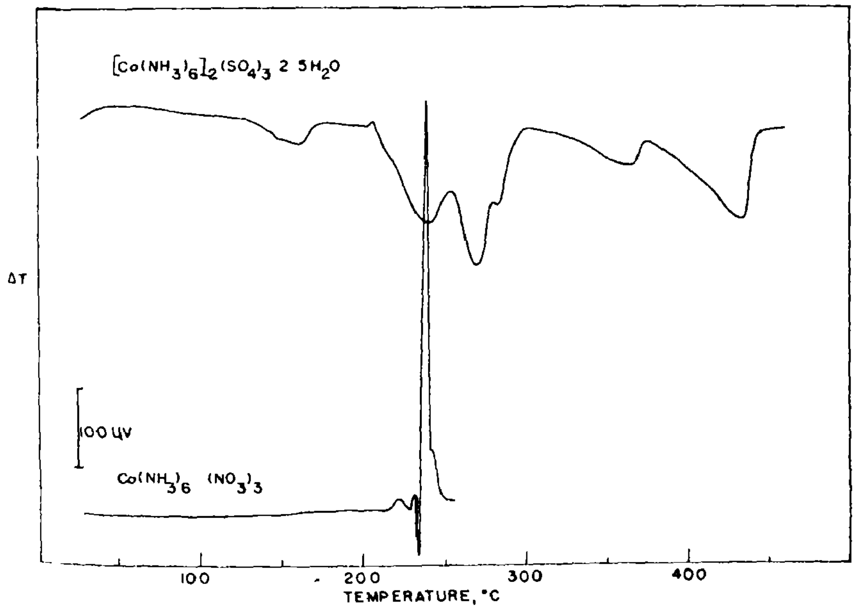


Fig. 2 Differential thermal analysis curves of hexamminecobalt (III) complexes

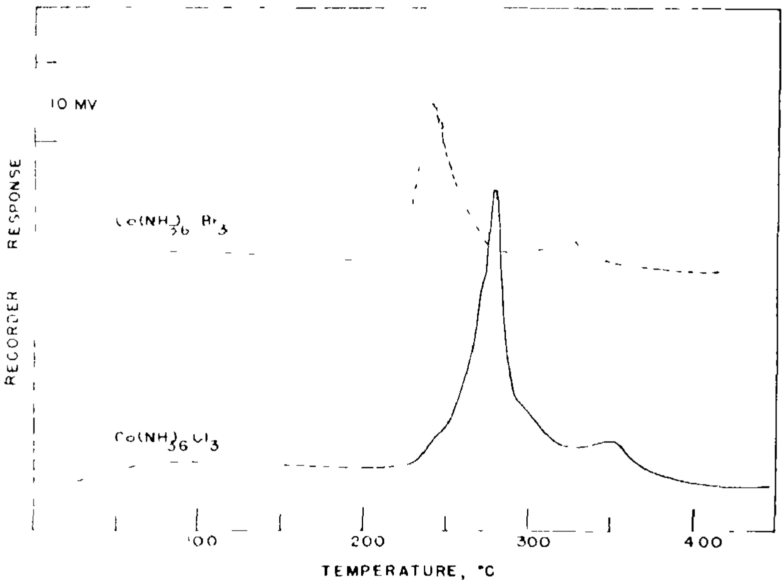


FIG. 3 Gas evolution curves of hexamminecobalt (III) complexes

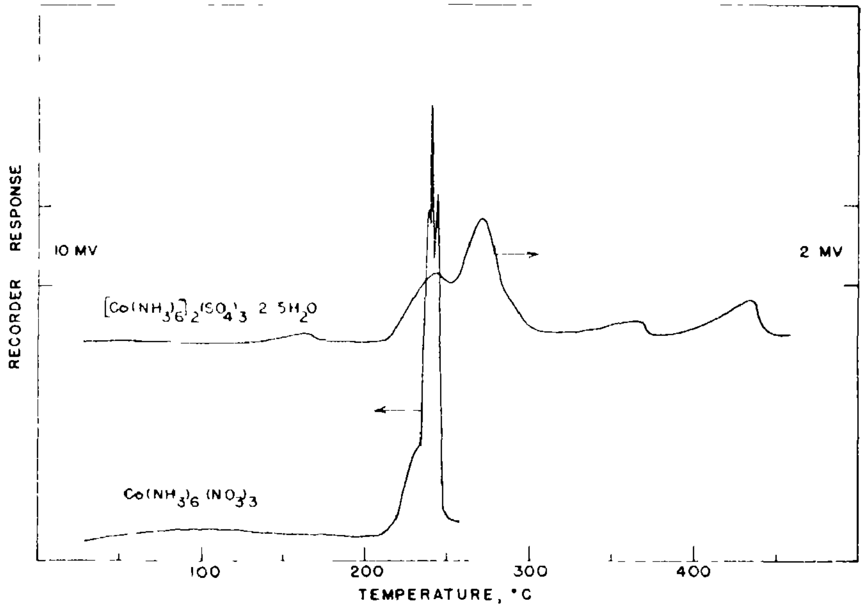


FIG. 4 Gas evolution curves of hexamminecobalt (III) complexes

temperatures previously reported in an ammonia atmosphere[1,3] The first endothermic peak maxima temperature was 280°, followed by a second broad peak between 300 and 375°C Only a small GE peak was noted in this latter temperature range which indicated that the decomposition product was either a slightly volatile substance such as ammonium chloride or that only a small amount of gas was evolved

Similarly, $[Co(NH_3)_6]Br_3$, began to decompose starting at about 200°C and gave two peaks with peak maxima temperatures of 240 and 325°C, respectively The G curve revealed that both of these endothermic peaks involved gaseous decomposition products, although the origin of the second GE peak may be the same as in the case of $[Co(NH_3)_6]Cl_3$.

The nitrate complex, $[Co(NH_3)_6](NO_3)_3$ gave two small exothermic peaks, at 220 and 230°C, respectively, followed by a sharp endothermic peak at 235°C, and then a large exothermic peak at 240°C. The highly exothermic nature of this reaction may be seen from this curve. The GE curve showed the presence of evolved gases from 210 to 250°C.

The sulphate complex, $[Co(NH_3)_6]_2(SO_4)_3 \cdot 2.5H_2O$, gave a rather complicated DTA curve. The first broad peak, centered at about 160°C, was rather difficult to interpret since a weight-loss curve showed that the compound was stable up to about 220°C. This peak may be caused by the evolution of a small amount of adsorbed water since the GE curve also had a small peak in this temperature range. The next series of endothermic peaks began at about 210°C, giving peak maxima temperatures of 240 and 270°C, respectively, with a shoulder peak at 280°C. Additional endothermic peaks were observed at 365 and 430°C, respectively. All of the reactions involved a gaseous decomposition product as evidenced by the GE curve.

Stoicheiometry of reaction. The results of the reaction stoicheiometry studies are given in Table 1.

From the data in Table 1, the compounds, $[Co(NH_3)_6]Cl_3$ and $[Co(NH_3)_6]Br_3$, decomposed according to the reactions

$$6[Co(NH_3)_6]Cl_3(s) \xrightarrow{He} 6CoCl_2(s) + N_2(g) + 6NH_4Cl(s) + 28NH_3(g) \qquad (1)$$

$$6[Co(NH_3)_6]Br_3(s) \xrightarrow{He} 6CoBr_2(s) + N_2(g) + 6NH_4Br(s) + 28NH_3(g) \qquad (2)$$

The decomposition stoicheiometry of $[Co(NH_3)_6]Cl_3$, in helium, was identical to that previously presented (2) except for the formation of the pentammine intermediate. The pentammine may only be formed if the pyrolysis is carried out in an ammonia atmosphere or at an extremely slow heating rate (3). As can be seen, the bromide dissociated in a manner similar to that of the chloride. In neither case was chlorine or bromine detected in the decomposition gases. The reducing agent for the Co(III) → Co(II) reaction is apparently ammonia although it was not possible to detect the transitory existence of the free halogens, had they been formed in the reaction.

A probable decomposition sequence which accounts for the thermal dissociation of the chloride or bromide complexes under the above experimental conditions is (X = Cl or Br)

$$6[Co(NH_3)_6]^{3+} + 18X^- \rightarrow 6[Co(NH_3)_5X]^{2+} + 12X^- + 6NH_3$$

$$6[Co(NH_3)_5X]^{2+} + 12X^- \rightarrow 6[Co(NH_3)_3X_3] + 12NH_3$$

$$6Co(NH_3)_3X_3 \rightarrow 6CoX_2 + 6NH_4X + N_2 + 10NH_3$$

Certainly, from the GE curve, the greater part of the ammonia is evolved in the [illegible] 300°C temperature range. The smaller GE peaks could result from the nitrogen and ammonia evolved in the last step.

The sulphate complex, $[Co(NH_3)_6]_2(SO_4)_3 \cdot 2.50H_2O$ decomposed in a manner

TABLE 1. REACTION STOICHIOMETRY DATA FOR THE HEXAMMINECOBALT (III) COMPLEXES *

Sample wt (mg)	Residue (%) Found	Residue (%) Calc	NH_3 (meq)	NH_3/Co ratio, Found	NH_3/Co ratio, Calc	N_2/NH_3 ratio†, Found	N_2/NH_3 ratio†, Calc
$[Co(NH_3)_6]Cl_3$							
70.68	48.60	48.55	1.224	4.63	4.67	0.0361	0.0357
57.88	48.63		0.991	4.58			
$[Co(NH_3)_6]Br_3$							
89.22	54.60	54.57	1.050	4.72	4.67	0.0364	0.0357
89.00	55.10		1.072	4.83			
$[Co(NH_3)_6]_2(SO_4)_3 \cdot 2.5H_2O$							
305.49	46.50	47.29	4.526	4.86	4.67	0.0392	0.0357
211.84	46.30		3.036	4.70			
				Water (%) Found	Water (%) Calc	H_2O/Co ratio, Found	H_2O/Co ratio, Calc
				7.17	2.87	2.61	2.50
				6.71		2.44	
$[Co(NH_3)_6](NO_3)_3$							
64.72	22.90	23.12	0.264	1.42	1.50	1.85	1.89
102.75	22.33		0.416	1.41			
		Water (%) Found	Water (%) Calc	H_2O/Co ratio, Found	H_2O/Co ratio, Calc	N_2O/NH_3 ratio†, Found	N_2O/NH_3 ratio†, Calc
		31.37	31.59	6.04	6.08	0.382	0.389
		31.20		6.01			

* Complexes heated at about 5 C per min up to a maximum temperature of 600

† Based upon mass spectrographic analyses

similar to that found for the chloride and bromide compounds. The data found agreed quite well with the reaction

$$6[Co(NH_3)_6]_2(SO_4)_3 \cdot 2.5H_2O(s) \xrightarrow{\text{He}} 12CoSO_4(s) + N_2(g) + 6(NH_4)_2SO_4(s) + 56NH_3(g) + 15H_2O(g) \quad (4)$$

The ammonia to cobalt ratio that was found agreed well with that found for the chloride and bromide complexes. No other gaseous decomposition product was found by mass spectrographic analysis. The decomposition sequence is probably the same as that for the chloride and bromide complexes.

The dissociation of the nitrate complex was decidedly more complex. The data found agreed well with the reaction

$$12[Co(NH_3)_6](NO_3)_3(s) \xrightarrow{\text{He}} 4Co_3O_4(s) + 18NH_3(g) + 7N_2O(g) + 73H_2O(g) + 4NH_4NO_3(s) + 34N_2(g) \quad (3)$$

Only the gaseous compounds as given in the above reaction could be detected by the mass spectrometer. Other oxides of nitrogen, such as NO and NO_2, were not detected

The N_2O in the decomposition gases was identified from the prominent peaks at m/e ratios of 44(100 0 per cent) and 30(31 1 per cent) This was confirmed from the literature(11) and from the spectrum of a known sample of N_2O

A possible decomposition sequence which accounts for the thermal dissociation is as follows

$$12[Co(NH_3)_6]^{3+} + 36NO_3 \rightarrow 12[Co(NH_3)_5NO_3]^{2+} + 24NO_3 + 12NH_3$$

$$12[Co(NH_3)_5NO_3]^{2+} + 24NO_3 \rightarrow 12[Co(NH_3)_4(NO_3)_2]^{+} + 12NO_3 + 12NH_3$$

$$7NO_3 + 7NH_3 \rightarrow 7N_2O + 7H_2O + 7OH^-$$

$$12[Co(NH_3)_4(NO_3)_2]^{+} + 5NO_3 + 7OH \rightarrow 4Co_2O_3\,CoO$$
$$+ 4NH_4NO_3 + NH_3 + 34N_2 + 66H_2O$$

This dissociation reaction is different from that previously obtained for the nitro-complexes, $[Co(NH_3)_5NO_2]Cl_2$ and $[Co(NH_3)_3(NO_2)_3]$, where only nitrogen, water and ammonia were found (2) However, the identification technique previously employed may not have been sensitive enough to detect other gases

Acknowledgements The helpful assistance of R G SEWELL T D GEORGE and J P SMITH is gratefully acknowledged This work was supported by the U S Air Force Office of Scientific Research through Contract No AF-49(638)-787

(11) Amer Petroleum Inst , Research Proj 44, serial no 96 Carnegie Inst Tech (1952)

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 553 to 555. Pergamon Press Ltd. Printed in Northern Ireland

PSEUDOMORPHIC DECOMPOSITION OF URANIUM PEROXIDE INTO UO_3

E. H. P. CORDFUNKE
Reactor Centrum Nederland, Petten, Netherlands
and
A. A. VAN DER GIESSEN
Philips Research Laboratories, Eindhoven, Netherlands

(*Received* 5 *October* 1962)

Abstract—In the decomposition of pure $UO_4 \cdot 4aq$ into amorphous UO_3, interesting pseudomorphism was observed by means of electron microscopy. If the peroxide contains small amounts of nitrate, thermal decomposition leads to crystalline α-UO_3, which transformation is accompanied by a change in size and shape of the particles.

IN a previous paper[(1)] it was reported that α-UO_3 can be formed by decomposition of $UO_4 \cdot 2aq$ containing some nitrate. The thermal decomposition of pure $UO_4 \cdot 2aq$ below 460°C, however, results in amorphous UO_3. These transformations were studied in greater detail by means of electron microscopy. The results presented in this paper, demonstrate an interesting case of pseudomorphism.

EXPERIMENTAL

Samples of $UO_4 \cdot 4aq$ were prepared as starting materials for the preparation of amorphous UO_3 or α-UO_3, by precipitation with hydrogen peroxide from a solution of uranyl nitrate.[(1)] In one series of preparations the precipitates were carefully washed with water, while in another series the washing procedure was omitted, the latter method leading to products containing some nitrate (up to 5 per cent). The precipitates, dried below 50°C, have the composition $UO_4 \cdot 4aq$.[(2)] Electron-microscope photographs were made, using a carbon replica technique in order to avoid heating of the sample by electron bombardment.

RESULTS AND DISCUSSION

We have studied the thermal decomposition of pure $UO_4 \cdot 4aq$ (series A) as well as of samples containing some nitrate (series B). The preparation is described in the experimental part. Electron-microscope photographs, together with X-ray diagrams, showed that the starting material ($UO_4 \cdot 4aq$) in both series consisted of the same crystalline needles (Fig. 1). The X-ray diagrams can be indexed by means of a monoclinic cell with $a = 11.85$ Å, $b = 6.79$ Å, $c = 4.25$ Å, $\beta = 93°37'$.[(3)] The shortest axis (c) is found to be along the length of the crystallites.

After heating product A for 2 hr at 80°C, $UO_4 \cdot 2aq$ is formed without change in size and shape of the particles (Fig. A-2). According to ZACHARIASEN[(4)] this material is

---

[(1)] E. H. P. CORDFUNKE, *J. Inorg. Nucl. Chem.* **23**, 285 (1961).

[(2)] T. SATO, *Naturwissenschaften*, 48 (1961), 668 and 693.

[(3)] C. DEBETS, *J. Inorg. Nucl. Chem.* In press.

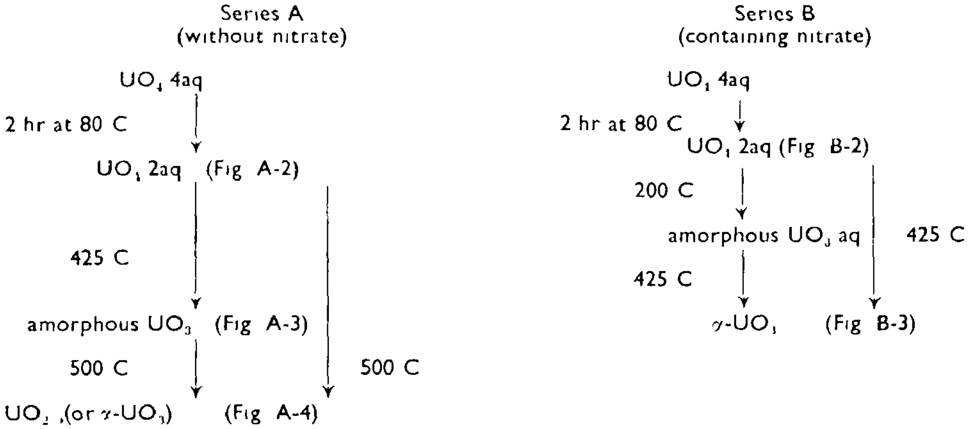
[(4)] W. H. ZACHARIASEN, C K-1367 (1944).

orthorhombic $a = 6.50$ Å, $b = 4.21$ Å, $c = 8.74$ Å. X-ray measurements showed the b-axis to be along the length of the needles. This product, when heated further to 400–450°C during 1–2 hr, decomposes to amorphous UO_3 but again no change in size and shape can be observed. This is shown in Fig. A-3. It is interesting to note the lines visible on the images of the particles after heating. We assume that these are in reality cracks formed by the escape of oxygen. The amorphous character of this UO_3 was revealed by the entirely diffuse Debye Scherrer X-ray diagrams. Some crystallinity is indicated by an electron-diffraction diagram (C-1). The small number of reflections which are to be seen in this figure may be due, however, to the exposure (3 sec 80 kV) of the particle to the electron beam (see below).

When the amorphous UO_3 is heated at 500°C a pseudomorphic crystallization takes place,* as revealed by a sharp X-ray diagram. The product, after prolonged heating, probably has the composition $UO_{2.9}$.(5) When this heating is carried out in less than two hours γ-UO_3 or a mixture of γ-UO_3 and $UO_{2.9}$ is obtained,(6) which can also be produced by rapid heating of product A-2 at 500°C (Fig. A-4). A long exposure of amorphous UO_3 to an electron beam (30 sec, 80 kV), probably on account of the heat generated, also causes crystallization, again without change in the general shape of the particles (Fig. C-3). The electron diffraction pattern obtained (Fig. C-2) is that of γ-UO_3.(7) From a number of these patterns of single needles it could be deduced that the c-axis is perpendicular to and the a-axis parallel to the length of the UO_3 needles, as indicated in Fig. C-3.

Samples of series B show a different behaviour. After heating (2 hr) at 80°C UO_4 2aq is again obtained, but now with particles of a completely different shape (Fig. B-2). When this sample is heated to 200°C an amorphous, hydrated UO_3 is formed, which on further heating (425°C) crystallizes to γ-UO_3, with retention of the shape of the particles. The same final (Fig. B-3) product can be obtained by heating product B-2 rapidly to 425°C. The scheme given below may illustrate the experiments.

Scheme



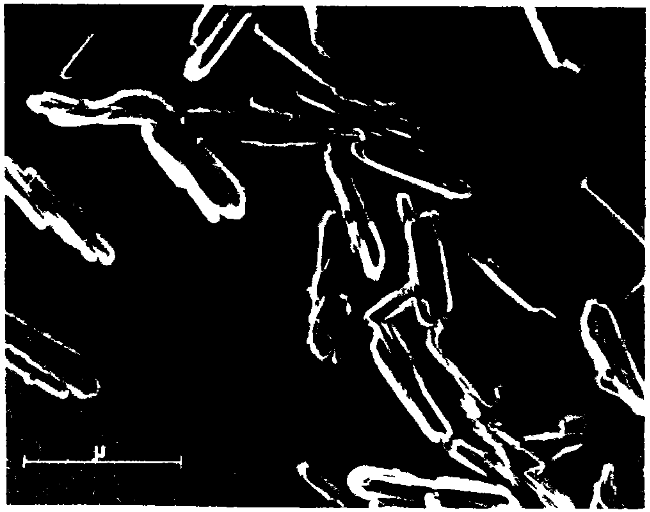
---

* The crystallization of amorphous UO_3 was confirmed by means of DTA-analysis, showing an exothermic crystallization peak at 480°C.

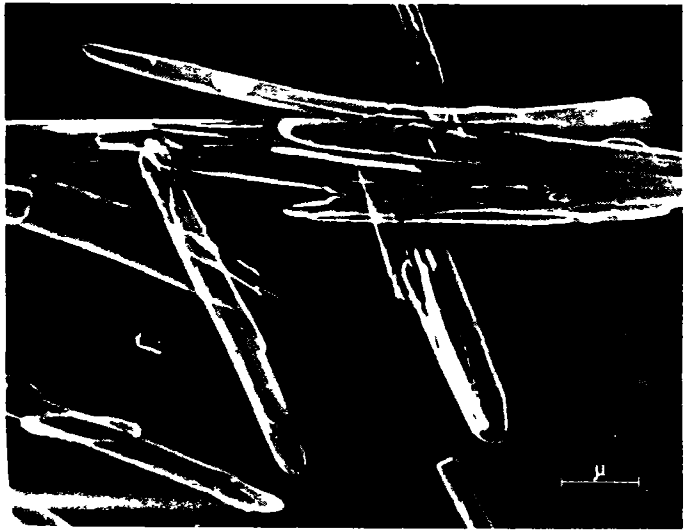
(5) H. R. HOEKSTRA and S. SIEGEL, *J. Inorg. Nucl. Chem.* **18**, 154 (1961).

(6) E. H. P. CORDFUNKE and P. ALING, *Rec. Trav. Chim.* In press.

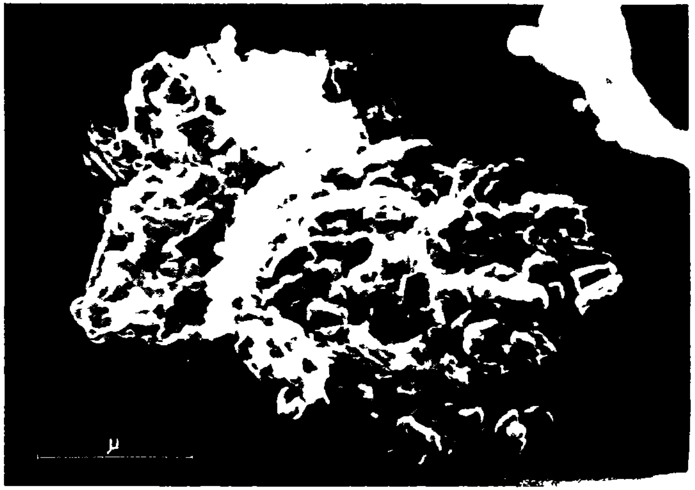
(7) W. H. ZACHARIASEN, *Acta Cryst.* **1**, 265 (1948).



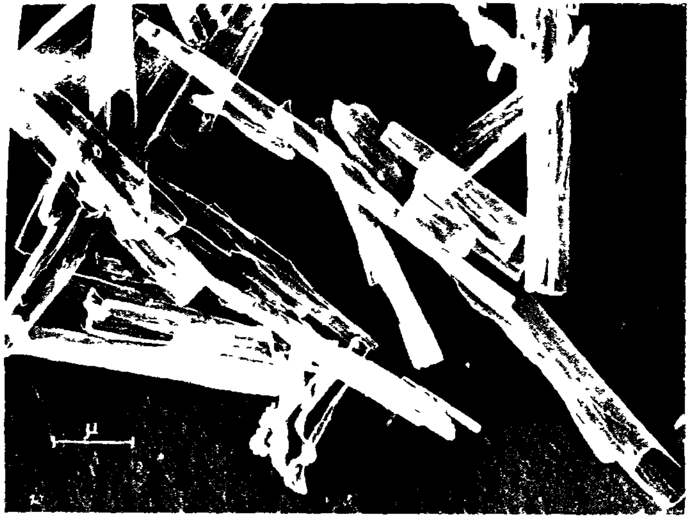
UO_3 4aq   Fig. 1



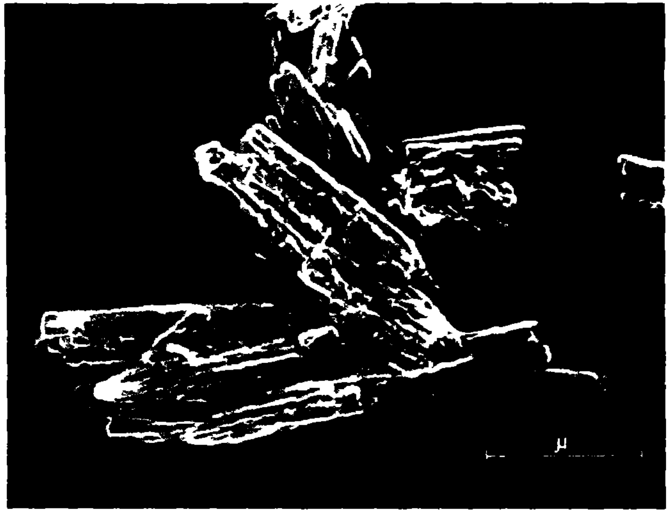
UO_3 2aq   A-2



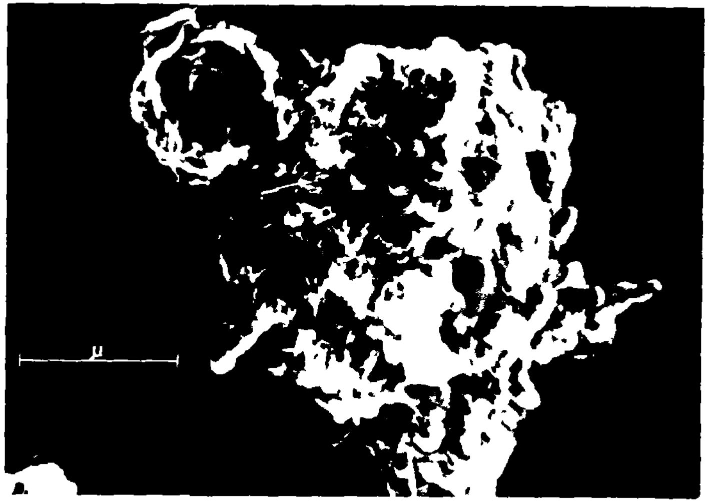
UO_3 2aq   B-2



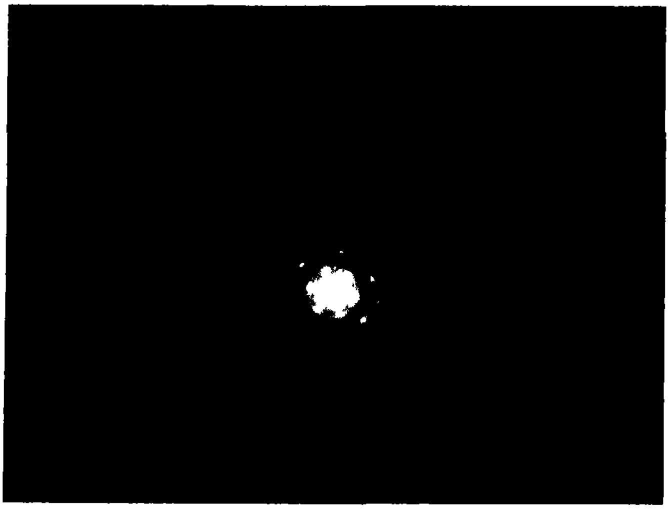
Amorphous UO$_3$ A-3



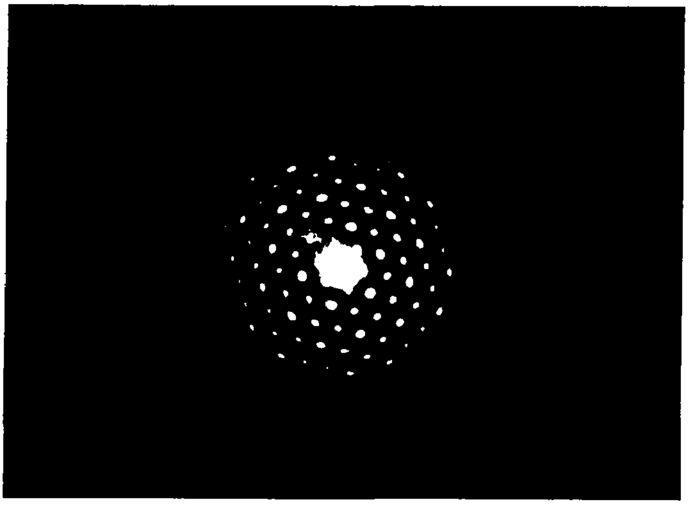
UO A-4



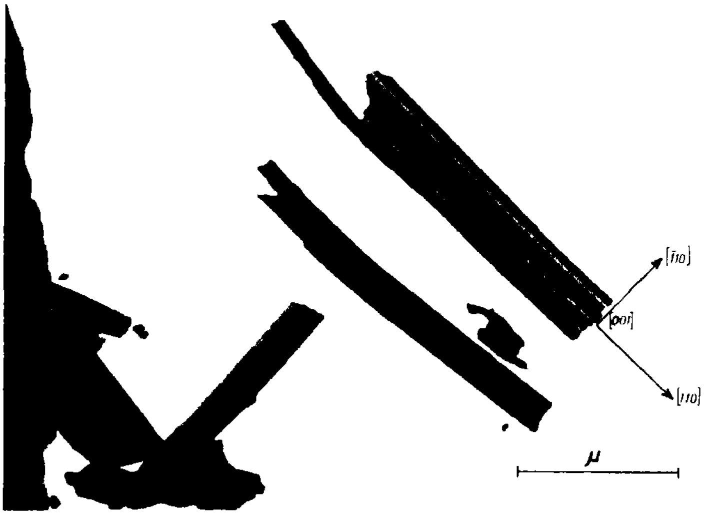
β-UO$_3$ B-3



C-1



C-2



C-3

Electron-diffraction photographs of amorphous UO_3 (C-1), the same sample after prolonged heati in the electron-beam (C-2) Electron-microscope photograph C-3 of the particle of sample C-1

The decomposition of pure UO_4 4aq into UO_4 2aq amorphous UO_3 and finally $UO_{2.9}$ via UO_4 2aq thus occurs pseudomorphically. If the starting material contains nitrate, however, the form of the crystallites changes during decomposition into UO_4 2aq at 80°C, but remains practically unchanged during the subsequent thermal decomposition into α-UO_3.

Acknowledgements. The authors wish to express their gratitude to Mr. H. B. HAANSTRA and his co-workers of the Philips' Research Laboratories for the careful way in which they prepared the electron-microscope photographs.

The authors are much indebted to Prof. Dr. J. A. GOEDKOOP and Dr. J. DE JONGE for valuable discussions.

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 557 to 558. Pergamon Press Ltd. Printed in Northern Ireland

DIMETHYLGERMANIUMSELENID

M. Schmidt und H. Ruf
Institut fur Anorganische Chemie der Universitat Marburg

(*Received* 2 *October* 1962)

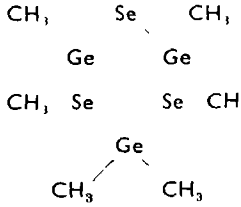
Abstract—Dimethylgermaniumdichloride reacts in benzene solution with sodium selenide, forming in good yields trimeric cyclic dimethylgermanium selenide $[(CH_3)_2GeSe]_3$ and sodium chloride.

E. G. Rochow(1) erhielt bei mehrtagiger Einwirkung von Schwefelwasserstoff auf Dimethyldichlorgerman in Wasser Dimethylgermaniumsulfid, uber dessen Molekulgrosse allerdings keine Angaben gemacht werden. Die Hydrolyse dieser Verbindung lieferte das ebenfalls noch unbekannte Dimethylgermaniumoxyd in tetramerer Form als Achtring.

Nachdem uns die Synthese eines ringformigen Diorganylzinnselenids(2) und ringformiger Diorganylsiliciumselenide(3) gelungen war, haben wir auch die Darstellung des Selen-analogons von Dimethylger-manium-oxyd und -sulfid versucht. Zu diesem Zweck wurde fein gepulvertes Natriumselenid (dargestellt aus den Elementen in flussigen Ammoniak(4)) unter Stickstoff-atmosphare in absolut trockenem Benzol im Molverhaltnis 1 : 1 mit Dimethyldichlorgerman umgesetzt. Bereits bei Raumtemperatur setzt eine Reaktion ein, die durch Ruckflusskochen vervollstandigt wird:

$$x(CH_3)_2GeCl_2 + x\,Na_2Se \rightarrow 2x\,NaCl + [(CH_3)_2GeSe]_x \qquad (1)$$

Die durch Abfiltrieren vom gebildeten Kochsalz getrennte gelbe benzolische Losung hinterlasst nach dem Abziehen des Losungsmittels ein zahflussiges gelbes Ol. Unter einem Druck von 2 Torr destilliert es zum grossen Teil oberhalb 90°C, wobei jedoch die Siedetemperatur dauernd ansteigt. Das prachtig gelb gefarbte, viskose Destillat erstarrt beim Abkuhlen zunachst zu einer wachsartigen festen Masse, aus der sich bei mehrstundigem Stehen grosse, rautenformige Kristalle abscheiden. Nach etwa 2 Tagen ist der grosste Teil des Destillats kristallin. Die farblosen Kristalle werden durch Abpressen zwischen Filtrierpapier vom anhaftenden Ol befreit. Analysen und kryoskopische Molekulargewichtsbestimmungen zeigen, dass es sich bei der Verbindung um trimeres Dimethylgermaniumselenid, also um einen Sechsring aus drei Germanium- und drei Selenatomen handelt.



---

[1] G. Rochow, *J. Amer. Chem. Soc.* **70**, 1801 (1948).
[2] Schmidt und H. Ruf, *Ber. Dtsch. Ges. Chem.* Im Druck.
[3] Schmidt und H. Ruf, *Z. Anorg. Chem.* Im Druck.
[4] Klemm, H. Sodomann und P. Langmesser, *Z. Anorg. Chem.* **241**, 281 (1939).

Im Gegensatz zum analog gebauten, geruchlosen trimeren Dimethylzinnselenid(2) riecht die Substanz recht unangenehm (Selenwasserstoff?) allerdings nicht so intensiv wie das dimere und trimere Dimethylsiliciumselenid,(3) was sicher mit der Bestandigkeit gegenuber Feuchtigkeit zusammenhangt Wahrend die Zinnverbindung selbst von kochendem Wasser nicht merklich angegriffen wird,(2) die Siliciumverbindung dagegen schon von feuchter Luft weitgehend zesetzt wird ist das bei 53 C schmelzende trimere Dimethylgermaniumselenid gegen kaltes Wasser noch ziemlich lange bestandig Erst beim Erwarmen mit Wasser tritt unter Zischen Hydrolyse ein, wobei Selenwasserstoff entsteht

Der gelbe wachsartige Destillationsruckstand loste sich, obwohl er aus benzolischer Losung erhalten wurde, nur noch teilweise in Benzol Es handelt sich dabei wohl um ein Gemisch verschiedener polymerer Dimethylgermaniumselenide, die bei der Destillationstemperatur aus der trimeren Verbindung entstanden sind Da dieses Gemisch nicht weiter gereinigt werden konnte, liefern die Analysen nur sehr ungenaue Werte

EXPERIMENTELLES

Sechs g Natriummonoselenid wurden unter Stickstoffatmosphare mit dem Ruhrmagneten fein zermahlen und mit 30 ml absolutem Benzol aufgeschlammt Unter Ruhren tropfte in der Folge eine Losung von 6 6 g Dimethyldichlorgerman (Kp 118 C) in 50 ml absolutem Benzol aus einem Tropftrichter langsam zu dieser Aufschlammung Die eingesetzten Mengen Selenid und Germaniumverbindung entsprechen einem Molverhaltnis von 1 1 Schon bei gewohnlicher Temperatur trat Reaktion ein wahrend sich die Reaktionslosung merklich erwarmte und die aufgeschlammten Feststoffe braun-rote Farbe annahmen Nach einer halben Stunde wurde das Reaktionsgut weitere 30 Minuten am Ruckfluss gekocht und dann erkalten lassen Die benzolische Losung liess sich mittels einer Glasfritte durch Filtration unter Luftausschluss von ausgeschiedenem Natriumchlorid trennen Letzteres war, vermutlich durch Selenabscheidung rosa gefarbt Das benzolische Filtrat war von intensiv gelber Farbe Nach der Destillation des Benzols blieb ein gelbes, unangenehm riechendes Ol als Ruckstand ubrig Dieses Öl destillierte im Vakuum bei 2 Torr zwischen 90 und 120 C als schone viskose, gelbe, durchscheinende Flussigkeit in die Vorlage Die Siedetemperatur war nicht konstant, sondern stieg weiter an Durch Destillation konnte keine normale Fraktionierung durchgefuhrt werden Daher wurde die Destillation unterbrochen nachdem die Siedetemperatur 120 C erreicht hatte Beim Stehen des zahflussigen gelben Destillats uber Nacht kristallisierte das Öl teilweise aus, wobei sich prachtige, rautenformige, durchsichtige Kristalle bildeten Diese Kristalle wurden mit dem Spatel aus dem Ol herausgenommen und das anhaftende Ol auf Filterpapier abgepresst So konnte das Produkt farblos erhalten werden Der Schmelzpunkt betrug 53 C Der kristalline Korper hat schwachen Geruch nach Selenwasserstoff und ist an der Luft bestandig Der bei der Destillation als Ruckstand verbliebene Teil erstarrte beim Erkalten und war von wachsahnlicher Konsistenz $C_6H_{18}Ge_3Se_3$ (544 8) ber C, 13 2, H, 3 1, Ge, 40 1, Se, 43 6 gef C, 13 8, H 3 2, Ge, 39 9, Se, 42 4 Molgewicht (kryoskopisch in Benzol) 521 5

Anerkennung -Der Union Miniere du Haut-Katanga, Brussel, danken wir fur kostenlose Uberlassung von Germaniummetall

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 559 to 566. Pergamon Press Ltd. Printed in Northern Ireland

AQUEOUS SYSTEMS AT HIGH TEMPERATURE—IX

INVESTIGATIONS ON THE SYSTEM Li_2SO_4–H_2SO_4–H_2O AND ITS D_2O ANALOGUE, 200–470°C. SOLUBILITIES AND CRITICAL PHENOMENA*[1]

WILLIAM L. MARSHALL, RUTH SLUSHER and FRED J. SMITH†
Reactor Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee

(*Received* 17 *September* 1962)

Abstract—The solubilities of Li_2SO_4 in H_2SO_4–H_2O and in D_2SO_4–D_2O solutions in equilibrium with vapour were determined at temperatures between 200 and 350°C, and at concentrations of free acid from 0 to 1.5 molal. Solubilities in H_2O media at 200° varied from 2.75 m in H_2O to 2.83 m in 0.85 m H_2SO_4, and at 350° from 0.118 m in H_2O to 2.38 m in 1.46 m H_2SO_4. Corresponding solubilities in D_2O media were from 10 to 40 per cent lower. The solubilities of stoicheiometric Li_2SO_4 in H_2O were in good agreement with those published recently by LIETSEVSKAYA and RAVICH. Temperatures of critical phenomena (where liquid = vapour) varying between 374° and 470° were determined visually for solutions of Li_2SO_4, D_2SO_4, and D_2O at concentrations of SO_3 from 0.02 to 2.5 molal and at molal ratios, m_{Li_2O}/m_{SO_3}, varying from 0 to approximately 0.5. At higher molal ratios than about 0.5 and at concentrations of SO_3 of approximately 0.05 m and above, Li_2SO_4 crystallized from the liquid phases. The formation of DSO_4^- ions can be responsible both for the high solubility of lithium in the supercritical fluid and, except at low SO_3 molalities, the limit of the critical curves to a maximum molal ratio near 0.5.

FEW aqueous systems involving SO_3 as one component and containing an excess of acid have been investigated at temperatures above 200°. Some detailed studies, however, have been made on alkali sulphate–H_2O and alkali sulphate–alkali hydroxide–H_2O systems more recently by RAVICH *et al.*[2] and earlier by SCHROEDER *et al.*[3]

Recently at this laboratory, in an investigation of the condensed system NiO–SO_3–H_2O and its D_2O analogue at temperatures up to 400°,[4] nickel sulphate was found to hydrolyse to form oxy-sulphate solids in solutions containing low concentrations of SO_3, even in those containing an excess of free H_2SO_4. Determinations of critical phenomena (where liquid = vapour) showed stable concentrations of the NiO component as high as 0.1 molal in a supercritical fluid 1.0 molal in SO_3. A study of the condensed system Li_2SO_4–H_2SO_4–H_2O and its D_2O analogue was considered desirable in order to compare the solubility relationships of a 1–2 electrolyte with those of the

---

* This paper is based upon work performed at Oak Ridge National Laboratory, which is operated by Union Carbide Corporation for the U.S. Atomic Energy Commission.

† Summer participant, 1960. Present Address: Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana.

[1] Previous Paper in Series: *The Solubility of* UO_3 *Hydrates in* HNO_3–H_2O *Solutions*, 25–350°C, 10^{-4} *to* 5 *m Nitrate*, W. L. MARSHALL and R. SLUSHER, *J. Inorg. Nucl. Chem.* **25**, 283 (1963).

[2] M. I. RAVICH, *Itogi Nauki Khim. Nauki, Akad. Nauk. S.S.S.R.* **4**, 122 (1959) (Review); M. I. RAVICH, F. E. BOROVAYA and V. YA. KETKOVICH, *Dokl. Akad. Nauk. S.S.S.R.* **77**, 617–20 (1951); M. I. RAVICH and F. E. BOROVAYA, *Sektora Fiz-Khim. Anal., Inst. Obshchei i Neorg. Khim. Akad. Nauk. S.S.S.R.* **26**, 229–41 (1955).

[3] W. C. SCHROEDER, A. GABRIEL and L. P. PARTRIDGE, *J. Amer. Chem. Soc.* **57**, 1539 (1935).

[4] W. L. MARSHALL, J. S. GILL and R. SLUSHER, *J. Inorg. Nucl. Chem.* **24**, 889 (1963).

2:2 electrolyte NiSO$_4$. Lithium sulphate was especially selected for study because of the anomalies in physical and chemical behaviour exhibited by lithium salts, its potentialities as an additive to sulphate-based aqueous, homogeneous-reactor fuels for inhibiting corrosion(5) and its ability to raise the temperature of appearance of liquid–liquid immiscibility.(6) It was believed that Li_2SO_4 would not hydrolyse to form oxy-salts in acidic media or in water, and that relatively high concentrations would be phase stable in supercritical fluids. Since there are practically no reports of investigations of solubilities in D_2O media at temperatures above 200°, the comparative study was made.

Solubilities of Li_2SO_4 in H_2O, D_2O, H_2SO_4–H_2O, and D_2SO_4–D_2O solutions are presented at temperatures from 200 to 350°. The solubilities of Li_2SO_4 in H_2O are compared to those published recently elsewhere.(7) Temperatures of critical phenomena are presented for solutions of Li_2SO_4, D_2SO_4, and D_2O at concentrations of SO_3 varying from 0.02 to 2.5 molal and at various molal ratios, m_{Li_2O}/m_{SO_3}, defined as R_{Li}.

EXPERIMENTAL

Lithium sulphate monohydrate of reagent grade, obtained from J. T. Baker Co. and used without additional purification, was dehydrated by heating in an oven at 170°. Light water was distilled and further purified by passage through a mixture of cation and anion exchange resins. After this procedure the H_2O gave a specific conductivity of about 10^{-7} Ω^{-1} cm^{-1}. Heavy water containing 0.3 wt per cent H_2O as an impurity was used in the experiments in D_2O media. As in previous procedures a small volume of chemically pure, 30 wt per cent H_2O_2 was added to the solutions contained in each pressure vessel. This decomposed at elevated temperature to produce an oxidizing atmosphere necessary for inhibiting corrosion and preventing reduction of sulphate. For the runs in H_2O solution 2 ml volumes of H_2O_2 were added to 25 ml of liquid. In most of the runs in D_2O, 0.25–0.50 ml volumes of H_2O_2 were added. However, in a few experiments at concentrations of D_2SO_4 above 1 molal 1 ml volumes were added. In order to correct for the small amount of H_2O originally present and later added as H_2O_2, linear-extrapolations were made to 100 per cent D_2O based on the solubilities of Li_2SO_4 in H_2O solution and those in solutions containing D_2O. This correction varied between 0.2 and 1 per cent; it was dependent upon the volume of H_2O_2 initially added to each solution and the relative difference in solubility in H_2O and D_2O media.

Other procedures were the same as used previously(4, 8) although samples of solid phases were obtained by a freeze-down method as well as by the removal from the pressure vessels after a run. In the freeze-down method, samples of solution and solid were sealed in glass capillary tubes. These tubes were held for 24 hr in a molten salt bath maintained at high temperature. The tubes were removed and dropped into a mixture of dry-ice and trichloroethylene in order to freeze quickly the contained sample. After this procedure the tubes were removed separately, their ends were broken and, as the liquid melted, the solids were isolated by vacuum filtration. The solids were sealed immediately in capillary tubes for identification by X-ray diffraction. The solubility experiments were carried out by the direct sampling method using equipment described elsewhere,(9) and the observation of critical phenomena and limits of phase stability by the synthetic method.(10)

Experiments by the synthetic method showed reversibility within a few seconds of critical phenomena with temperature. Supersaturation was observed for the formation of Li_2SO_4 solid phase

---

(5) J. C. Griess and E. G. Bohlmann, U.S. Pat. 2950167 (to U.S. Atomic Energy Commission Aug. 23, 1960); *Chem. Abstr.* **55**, 344C (1961).

(6) H. F. McDuffie, Review in *Fluid Fuel Reactors*, (Edited by J. A. Lane, H. G. MacPherson, F. Maslan) Chap. 3, pp. 85–129. Investigations by R. S. Greeley, S. R. Buxton and J. C. Griess. Addison Wesley, Reading, Mass. (1958).

(7) V. M. Felnevskaya and M. I. Ravich, *Zh. Neorg. Khim.* **6**, 2380–6 (1961).

(8) W. L. Marshall and J. S. Gill, *J. Inorg. Nucl. Chem.* **22**, 115 (1961).

(9) J. S. Gill and W. L. Marshall, *Rev. Sci. Instrum.* **32**, 1060 (1961).

(10) C. J. Barton, G. M. Hebert and W. L. Marshall, *J. Inorg. Nucl. Chem.* **21**, 141 (1961).

Nevertheless, upon lowering the temperature the redissolving of solid phase within several minutes was used as one criterion of time to be allowed for the runs made by the direct sampling method. These latter runs were made for periods of time varying from 1½ hr to 3 days at each temperature. Analyses of solution phases as a function of time showed that equilibrium was fully established within 1½ hr.

Analyses of solution phases were performed by acid-base titrations both of excess H_2SO_4 and of total sulphate after removing lithium by means of Dowex-50 cation exchange resin. Densities of solution phases were determined at 25 ± 2° using a 1 cm^3 pycnometer. Since most analyses were made on pipetted volumes the densities were used to convert molar quantities to molalities. The experimental densities of the samples in D_2O solvent containing small amounts of H_2O impurity were linearly extrapolated to values in 100 per cent D_2O solvent by the same method as used for the solubilities. Densities were not determined for about 15 per cent of the samples in H_2O media, but were obtained from smoothed curves of experimental densities plotted against the molar concentration of H_2SO_4.

RESULTS AND DISCUSSION

The two-component system Li_2SO_4–H_2O *and its* D_2O *analogue*

Experimental values for the solubilities of Li_2SO_4 in H_2O and in D_2O solutions taken from Tables 1 and 2 are shown graphically in Fig. 1. Our results in light water are in good agreement with those of ELLNEVSKAYA and RAVICH[7] which are also included in Fig. 1. Furthermore, they have established that anhydrous Li_2SO_4 is the stable solid phase above 233°, the temperature which they found for the transition

TABLE 1 — THE SOLUBILITY OF Li_2SO_4 IN H_2SO_4–H_2O SOLUTIONS, 200–350°C*

H_2SO_4 (*m*)	Li_2SO_4 (*m*)	Density at 25°C	H_2SO_4 (*m*)	Li_2SO_4 (*m*)	Density at 25°C
t 200			*t* 300		
0	2.748	1.209_3	0	1.022†	
0.089	2.728	1.215_5	0.089	1.096	1.104_5
0.184	2.728	1.218_0	0.463	1.499	1.145_0
0.460	2.752	1.277_0	0.643	1.705	1.165_5
0.640	2.774	1.234_1	0.843	1.939	1.187_5
0.847	2.829	1.243_1	1.057	2.289	1.209_6
			1.333	2.531	1.236
t 235			*t* 325		
0	2.633	1.205_6	0	0.425	1.040_1
0.082	2.634	1.209_5	0.275	0.763	1.082_9
0.431	2.615	1.218_7	0.465	1.076	1.114_1
0.604	2.640	1.225_0	0.915	1.766	1.179_7
0.795	2.700	1.233_0	1.175	2.119	1.211_0
0.960	2.773	1.241_7	1.349	2.366	1.231
t 270			*t* 350		
0	1.975	1.159_6	0	0.118	1.008_0
0.084	1.951	1.165_0	0.308	0.538	1.065_4
0.446	2.074	1.184_0	0.525	0.880	1.102_0
0.611	2.180	1.193_8	0.705	1.192	1.131_2
0.812	2.312	1.204_6	1.028	1.701	1.179_0
0.994	2.449	1.218_0	1.289	2.124	1.214_7
1.307	2.706	1.247_3	1.461	2.383	1.235_9

* The solid phases are $Li_2SO_4 \cdot H_2O$ at 200° and Li_2SO_4 anhydrous, at all other temperatures.

† Extrapolated value.

TABLE 2. THE SOLUBILITY OF Li_2SO_4 IN D_2SO_4–D_2O SOLUTIONS, 200–350 °C*

D_2SO_4 (m)	Li_2SO_4 (m)	Density at 25 °C	D_2SO_4 (m)	Li_2SO_4 (m)	Density at 25 °C
t = 200			t = 300		
0	2.304	1.297	0	0.700	1.171_2
0	2.279	1.299_0	0	0.686	1.172_0
0.160	2.260	1.301	0.153	0.814	1.188_1
0.500	2.262	1.311_9	0.292	0.964	1.206_2
0.743	2.331	1.320_1	0.468	1.196	1.231_0
1.052	2.433	1.337_1	0.711	1.471	1.260_2
1.582	2.711	1.382	0.881	1.670	1.280_2
			1.091	1.905	1.303_7
t = 235			t = 325		
0	2.131	1.287_6	0	0.239	1.133_2
0	2.143	1.287_1	0.095	0.343	1.147_6
0.149	2.118	1.291_0	0.293	0.608	1.179_6
0.282	2.128	1.292_0	0.744	1.256	1.249_9
0.458	2.125	1.300_0	1.007	1.629	1.285_0
0.688	2.189	1.308_5	1.327	2.135	1.321_0
1.047	2.362	1.330_9	1.507	2.288	1.343_7
1.452	2.545	1.365_0			
t = 270			t = 350		
0	1.413	1.232_2	0	0.069	1.115_3
0	1.394	1.233_6	0.121	0.215	1.136_1
0.150	1.462	1.241_0	0.360	0.537	1.176_8
0.286	1.503	1.248_8	0.881	1.289	1.257_3
0.467	1.599	1.261_9	1.198	1.777	1.300_8
0.703	1.774	1.280_5	1.516	2.244	1.338_6
0.867	1.939	1.298_2			
1.069	2.086	1.317_1			

---

* The solid phases are $Li_2SO_4 \cdot D_2O$ at 200 °C and Li_2SO_4, anhydrous, at all other temperatures.

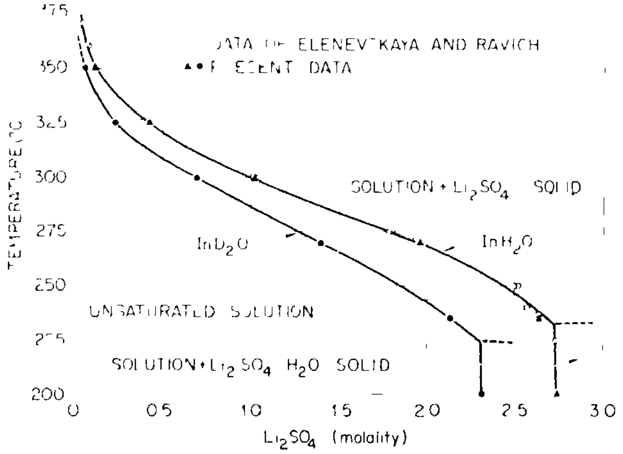


FIG. 1. Solubilities in the System Li_2SO_4–H_2O and its D_2O analogue, 200–370 °C.

from the monohydrate Our own X-ray diffraction patterns, obtained on solid in equilibrium with liquid at 250° and removed by the freeze-down method, showed both the anhydrous Li_2SO_4 and the monohydrate (or monodeuterate) in both the H_2O and D_2O systems, and in those systems containing acid At 200° only the monohydrate was identified The patterns obtained for solids removed form the pressure vessels after runs at all temperatures showed only the monohydrate Apparently, rapid hydration of the anhydrous salt occurred upon cooling the mixtures in the pressure vessels to 25° but the anhydrous phase observed using the freeze-down method confirms the results of ELENEVSKAYA and RAVICH

The solubility of Li_2SO_4 in H_2O and D_2O solution shows the retrograde solubility with increasing temperature which is characteristic of many other sulphate salts[3,11] Its solubility is decreased in D_2O compared to that in H_2O solvent

The three-component system Li_2SO_4–H_2SO_4–H_2O *and its* D_2O *analogue*

The experimentally determined solubilities of Li_2SO_4 in various concentrations of H_2SO_4 at different temperatures are given in Table 1 and shown graphically in Fig 2

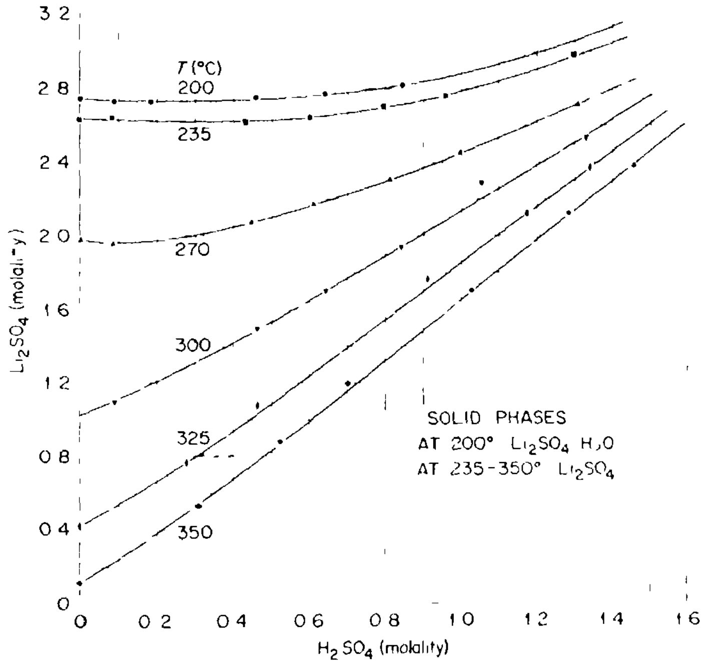


FIG 2 —Solubilities in the system Li_2SO_4 H_2SO_4 H_2O 200 350 C

Included also in the table are densities at 25 In contrast to the behaviour of the 2–2 electrolyte, $NiSO_4$, stoicheiometric Li_2SO_4 is stable in water as well as in dilute solutions of H_2SO_4 The solubility curves show the same general characteristics of those for $NiSO_4$ over the region of H_2SO_4 concentration where $NiSO_4$ H_2O is the separating solid The solubility increases as a function of increasing H_2SO_4 concentration and decreases with temperature

---

See the numerous papers of A BENRATH and others *Z Anorg Chem* (1924-1941), H S BOOTH and R M BIDWELL, *J Amer Chem Soc* **72**, 2567 (1950)

Analogous solubilities in D_2SO_4 D_2O solutions are presented in Table 2, which also includes densities at 25 , and are shown graphically in Fig 3 All solubilities and densities have been corrected to correspond to values in 100 per cent D_2O by linear extrapolation At constant temperature, solubilities in D_2O are lower than those in H_2O These differences are considered to be caused by a first order effect of solvent

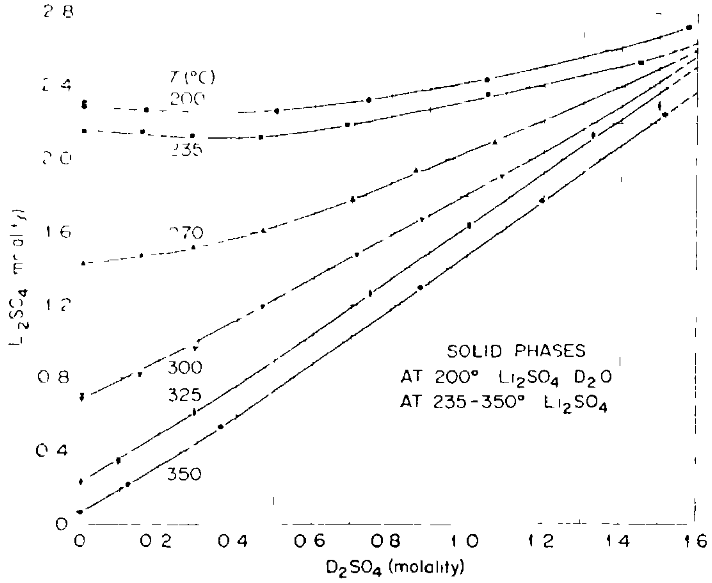


FIG 3 —Solubilities in the system Li_2SO_4–D_2SO_4 D_2O, 200–350 C

There is an approach on a percentage basis of the solubility of Li_2SO_4 in D_2SO_4-D_2O to that in H_2SO_4-H_2O as the concentration of acid is increased A cross-over in the two solubilities (observed for the system NiO–SO_3–H_2O[1]) was not observed probably because of the high solubility of Li_2SO_4 in the solvent alone

Dense supercritical fluids containing Li_2SO_4, D_2SO_4 *and* D_2O, *critical phenomena*

Observed temperatures of critical phenomena, i e , the temperature at which the composition of liquid becomes identical with that of vapour, are given in Table 3 for various compositions of Li_2SO_4, D_2SO_4 and D_2O Included also are temperatures at R_{Li} - 0 reported previously[12] No extrapolation was made to obtain values in 100 per cent D_2O—the D_2O contained approximately 0 3 per cent H_2O impurity The meniscus was observed to disappear at tube fillings of approximately 50-70 volume per cent The values are believed to approximate within a few degrees the true critical temperatures, which can only occur at a liquid volume filling of 50 per cent The critical temperatures are plotted in Fig 4 and show that considerably higher concentrations of Li_2SO_4 are soluble in the supercritical fluid than were found for $NiSO_4$ in H_2SO_4-H_2O fluids At 0 02 m SO_3, Li_2SO_4 as a stoicheiometric salt (R_{Li} - 1) is soluble in the supercritical fluid

Included in Table 3 are temperatures at which a solid phase was observed to crystallize from solutions contained in sealed tubes The synthetic tube compositions

---

[12] W L MARSHALL, E V JONES, G M HEBERT and F J SMITH, *J Inorg Nucl Chem* **24**, 995 (1962)

TABLE 3 —TEMPERATURES (°C) FOR THE APPEARANCES OF CRITICAL PHENOMENA AND PRECIPITATIONS OF SOLID PHASES IN THE SYSTEM Li_2O-SO_3-D_2O

Molal Ratio, m_{Li_2O}/m_{SO_3}	SO_3 (m) 2.500	2.000	1.000	0.600	0.400	0.2000	0.1000	0.0500	0.02000
1.000	204^s	250^s	274^s	299	306^s	311^s	321^s	334^s	374
0.800	227^s	263^s	288^s	313	323	330^s	338^s	348^s	374
0.650	265^s	295^s	321^s	344^s	353	356^s	363^s	367^s	373
0.500	347^s	389^s	418	400	391	386	380	375	373
0.300	--	445	412	394	387	382	377	374	372
0.2000	466	438	411	393	386	379	375	373	372
0.1000	458	434	410	392	385	379	375	374	372
0.0500	456	432	409	392	385	379	375	373	372
0		—	408	392	385	379	376	373	372

s - Precipitation of Solid Phase (experimentally estimated)

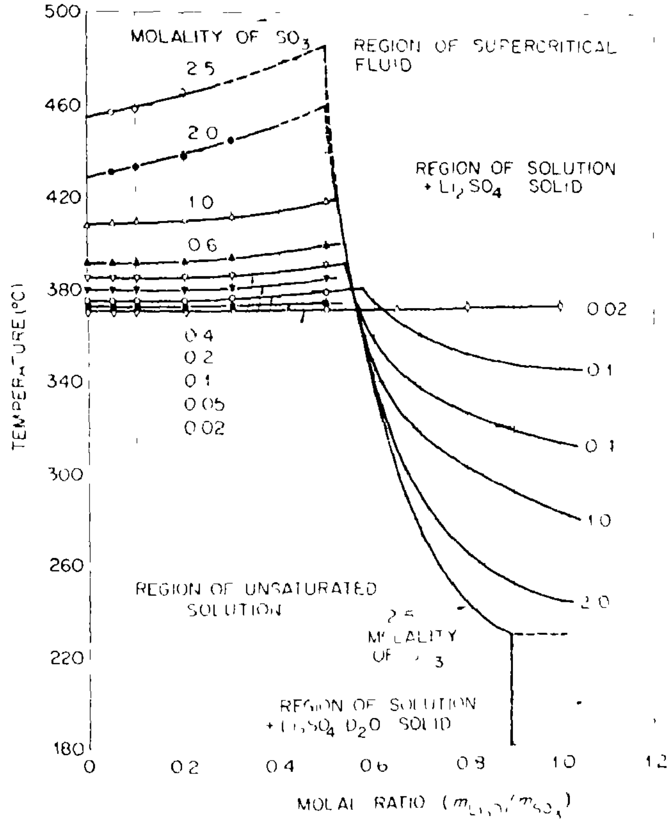


FIG. 4 —Critical phenomena and solid-liquid phase boundaries in the system Li_2O-SO_3-D_2O

are room temperature compositions and, therefore, should not be expected to agree precisely with the analytical data obtained by sampling at the equilibrium temperature. The results were believed to differ from the analytical values chiefly because of supersaturation and failure to maintain near equilibrium conditions upon cooling the tubes. The equilibration of mixtures containing a *solid phase* by means of the vibro tool when the tube is held vertically,[10] as in this work, is less effective than when it is held horizontally.[13] Curves derived from data obtained by the direct sampling method (Table 2) are included on Fig. 4 and are considered to represent the best values for the true solubilities since equilibrium was established and consideration of loss of components to the vapour phase was unnecessary.

At temperatures between 375 and 425° the formation of DSO_4^- ions can account for the high solubility of Li_2SO_4 in the supercritical SO_3–D_2O and, with the exception of solutions 0.02 m in SO_3, the limit of R_{Li} in the vicinity of 0.5. In a study at lower temperature[11] the constant for the dissociation, $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$ has been shown to decrease considerably with temperature reaching a value of about 1.24 × 10^{-5} at 225°.

Visual observations at saturation vapour-pressures showed the absence of a second-liquid phase which has been observed for sulphate containing systems such as UO_3–SO_3–H_2O[15] and $CuSO_4$–H_2SO_4–H_2O.[16] At 400° and 422 bars, and at 500° and 653 bars, however, MOREY and CHEN[17] have found that Li_2SO_4 solid can be dissolved in water solution in contact with supercritical fluid, and therefore additional study on this system at high temperatures and pressures will be of considerable interest.

---

[10] W. L. MARSHALL, H. W. WRIGHT and C. H. SECOY, *J. Chem. Educ.* **31**, 34 (1954).

[11] M. H. LIETZKE, R. W. STOUGHTON and T. F. YOUNG, *J. Phys. Chem.* **65**, 2247 (1961).

[15] E. V. JONES and W. L. MARSHALL, *J. Inorg. Nucl. Chem.* **23**, 287 (1961); C. H. SECOY, *J. Amer. Chem. Soc.* **72**, 3343 (1950).

[16] E. E. CLARK, J. S. GILL, R. SLUSHER and C. H. SECOY, *J. Chem. Engng. Data* **4**, 12 (1959).

[17] G. W. MOREY and W. T. CHEN, *J. Amer. Chem. Soc.* **78**, 4250 (1956).

J Inorg Nucl Chem 1963 Vol 25 pp 567 to 574 Pergamon Press Ltd Printed in Northern Ireland

THE REACTION OF FERRIC IRON WITH ORTHO-PHOSPHATE

H GALAL-GORCHEV and W STUMM*
Division of Engineering and Applied Physics Harvard University,
Cambridge 38, Massachusetts

(*Received* 9 *July* 1962, *in revised form* 24 *September* 1962)

Abstract –The iron (III) orthophosphate system has been investigated spectrophotometrically and potentiometrically In dilute acid solutions the existence of $\mathrm{FeH_2PO_4^{2+}}$ and $\mathrm{FeHPO_4^+}$ can be established The stability of these two complexes has been determined at μ 0 4 and 25 C Qualitative evidence for the presence of higher and polynuclear phosphato-iron complexes is presented The conditions under which iron (III) phosphate precipitates have been studied

THE nature and properties of phosphate iron (III) complexes have been the objective of a considerable number of investigations by various workers,(1–6) but there is no general agreement among the reported results Values reported(7–10) for the solubility product of iron (III) phosphate are inconsistent and vary over a range of 10^{13} In order to establish the $\mathrm{FePO_4}$ solubility, the formation of soluble phosphato-iron complexes must be taken into account

This paper presents the results of an investigation of the iron (III) orthophosphate system by both spectrophotometric and potentiometric means The ferrous–ferri cell(11) and absorbance data were used in order to determine the stability of $\mathrm{FeH_2PO_4^{2+}}$ and $\mathrm{FeHPO_4^+}$, respectively In addition some experiments were carried out to elucidate the conditions for $\mathrm{FePO_4}$ precipitation All measurements were made in a $\mathrm{NaClO_4}$ medium of ionic strength 0 40 0 42 at 25 C Experimental conditions were selected under which the dimerization of $\mathrm{FeOH^{2+}}$ (12) and the hydrolysis of Fe(II) are negligible Since the experimental data gave evidence for the formation of higher and polynuclear phosphato iron (III) complexes in most of the experiments the concentrations of iron (III) and phosphoric acid were chosen so as to prevent these complications

EXPERIMENTAL

Reagents All reagents used were of analytical grade All solutions were prepared using doubly glass-distilled water Phosphoric acid sodium dihydrogen phosphate and perchloric acid solutions were standardized potentiometrically using standard carbonate-free sodium hydroxide

---

* To whom correspondence concerning this paper should be addressed

K A JENSEN *Z Anorg Chem* **221,** 1 (1934)

O E LANFORD and S J KIEHL *J Amer Chem Soc* **64,** 291 (1942)

J E SALMON *J Chem Soc* 2644 (1953), R F JAMESON and J E SALMON *ibid* 28 (1954) A HOLROYD and J E SALMON, *ibid* 269 (1956) 959 3239 (1957)

A RAM A K BOSE and S KUMAR *J Sci Industr Res (India)* **13** B 217 (1954)

A I PILIPENKO and L N IVASCHENKO *Zh Obshchei Khim*, **26,** 656 (1956)

S BANERJEE, *J Indian Chem Soc* **27,** 417 (1950)

C V COLE and M L JACKSON *J Phys and Colloid Chem* **54,** 128 (1950)

L H N COOPER, *J Mar Biol Ass U K* **27,** 314 (1947, 1948)

G ZHAROVSKII, *Trudy Komissii Anali Khim Akad Nauk S S S R* **3,** 101 (1951)

W M LATIMER, *Oxidation Potentials* Prentice Hall, New York (1952)

R E CONNICK, L G HEPLER, Z Z HUGUS JR , K W KURY W M LATIMER and MAAK-SANG TSAO *J Amer Chem Soc* **78,** 1827 (1956)

R M MILBURN, *J Amer Chem Soc* **79,** 537 (1957)

Stock solutions of iron (III) were prepared by dissolving appropriate quantities of hydrated ferric perchlorate (G. Frederick Smith) in 0.01 M perchloric acid to give 4×10^{-4}–8×10^{-4} M iron (III) solutions. The concentration of iron (III) was determined after dilution in 0.01 M $HClO_4$ to concentrations of less than 10^{-4} M from absorbance measurements at a wave length of 272 mμ, the isobestic point of the Fe^{3+}–$FeOH^{2+}$ equilibrium. A molar absorptivity of 1.60×10^{3} was used. This value was determined on Fe(III) solutions which have been standardized by potentiometric titration with EDTA. Ferrous perchlorate solutions were prepared by dissolving hydrated ferrous perchlorate (G. Frederick Smith) in 10^{-2} M $HClO_4$. Nitrogen used in the potentiometric work was further purified by passing through hot copper tube, sodium hydroxide, sulphuric acid solutions and finally through distilled water. Sodium perchlorate (G. Frederick Smith) was used for ionic strength adjustments.

Spectrophotometric measurements. Absorbance measurements were made with a Beckman Model DU Spectrophotometer. Spectra were obtained with a Beckman DK-2 Recording Spectrophotometer. Cells of 2, 5, and 10 cm light path were used. After mixing, the solutions were stored in a constant temperature bath prior to the absorbance measurements. Although the cell compartment was not thermostated, temperature was kept constant within 0.5° at 25°C.

Potentiometric measurements. These were made with a Rubicon precision type B potentiometer. The cell consisted of a bright platinum spiral electrode (10 cm^2 area) and a calomel reference electrode. Contact between the calomel electrode and the solution was made with a junction filled with 2M $NaNO_3$. One-hundred millilitre aliquots of stock solutions containing the desired concentrations of $Fe(ClO_4)_2$, $Fe(ClO_4)_3$, $HClO_4$ and $NaClO_4$ were pipetted into the cell compartment. Purified nitrogen was passed through the solutions. The stirrer was activated and after observing constant potential readings, standard phosphoric acid solution was added to the cell with a micropipette. The potential was read after each addition. The stirrer was left on while reading the potential. The potentials became constant approximately 2 min after each addition. In each experiment from 4 to 12 e.m.f. determinations were made at different phosphate concentrations.

Hydrogen ion concentration was generally computed from the amount of standard $HClO_4$ added to the solution. In those cases where H^+ contribution due to the hydrolysis of Fe^{3+} and H_3PO_4 and from complex formation were not negligible, measurement of hydrogen ion concentration was made with a Beckman Model G pH Meter. The electrode system was calibrated with solutions of known concentration of $HClO_4$ which were adjusted to the appropriate ionic strength with $NaClO_4$, the observed pH meter reading being compared with the actual hydrogen ion concentration.

Acidity constant of Fe^{3+} *and* H_3PO_4. Incidental to the main purposes of this investigation the absorption spectra of Fe(III) at $\mu = 0.4$ and at various (H^+) have been obtained (Fig. 1). For this ionic strength the first hydrolysis constant of Fe^{3+} has been calculated using the method of MILBURN and VOSBURGH[13]. A value of 1.9×10^{-3}, which is in good agreement with values reported by these authors, was obtained and was used in the subsequent calculations.

The first and second concentration acidity constants of H_3PO_4 were determined by potentiometric titration with NaOH in a $\mu = 0.4$, ($NaClO_4$) medium, and found to be, at 25°C: $K_{H_3PO_4} = 1.30 \times 10^{-2}$, $K_{H_2PO_4} = 2.40 \times 10^{-7}$.

ANALYSIS OF SPECTROPHOTOMETRIC DATA

Fig. 1 gives ultra-violet absorption spectra for ferric perchlorate solutions at various (H^+) and shows the effect of phosphate on the light absorption. For the evaluation of the complex formation equilibria, absorption measurements at a wave length of 272 mμ were analysed. This wave length corresponds to the isobestic point of the Fe^{3+}–$FeOH^{2+}$ equilibrium. The data were treated by using a modification of a method described by NEWTON and ARCAND[14]. The experimental results may be interpreted by considering the following equilibria:

$$Fe^{3+} + H_3PO_4 \rightleftharpoons FeH_nPO_4^{n+} + (3-n)H^+ \qquad Q_n \tag{1}$$

$$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+ \qquad Q_H \tag{2}$$

---

[13] R. M. MILBURN and W. C. VOSBURGH, *J. Amer. Chem. Soc.* **77**, 1352 (1955).

[14] T. W. NEWTON and M. G. ARCAND, *J. Amer. Chem. Soc.* **75**, 2449 (1953).

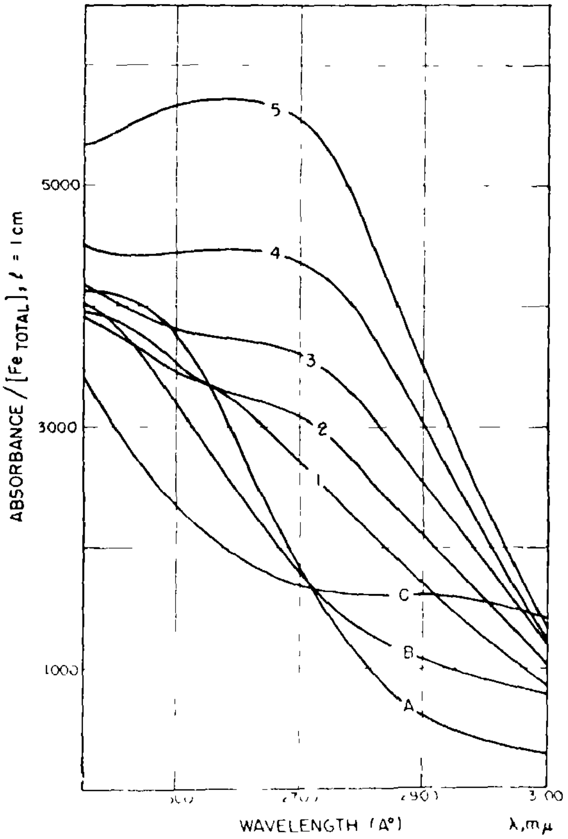


Fig. 1 — Effect of H$^+$ and H$_3$PO$_4$ on spectra of ferric perchlorate solutions
(Fe-III$_T$) in all solutions 3.5 × 10^{-4} M
log [H$^+$] A, 1.94, B 2.22, C 2.70, 1–5, 1.94 to 1.85
Total phosphorus A, B and C 0
1, 4.8 × 10^{-4} M, 2, 1.44 × 10^{-3} M, 3, 4.79 × 10^{-3} M, 4, 4.79 × 10^{-2} M, 5, 2.4 × 10^{-1}

The Q's are equilibrium quotients, for example

$$Q_H = \frac{(\mathrm{FeOH}^{2+})(\mathrm{H}^+)}{(\mathrm{Fe}^{3+})}$$

where ( ) signifies concentration in moles/l. If we define the following connotations for absorbances at 272mμ: A_0 = absorbance measured in absence of phosphate, A_1 = hypothetical absorbance if all the iron (III) were in the form of FeH$_n$PO$_4$, A = total absorbance, l = length of cell, then, for solutions containing identical concentrations of total Fe(III) and H$^+$

$$A/l = \varepsilon_{\mathrm{Fe}}[(\mathrm{Fe}^{3+}) + (\mathrm{FeOH}^{2+})] + \varepsilon_{\mathrm{FeH}_n\mathrm{PO}_4}(\mathrm{FeH}_n\mathrm{PO}_4^{n+}) \tag{3}$$

$$A_1/l = \varepsilon_{\mathrm{FeH}_n\mathrm{PO}_4}(\mathrm{Fe}_T) \tag{4}$$

$$A_0/l = \varepsilon_{\mathrm{Fe}}(\mathrm{Fe}_T) \tag{5}$$

where $\varepsilon_{\mathrm{Fe}}$ is the molar absorbance of Fe^{3+} at 272mμ, $\varepsilon_{\mathrm{FeH}_n\mathrm{PO}_4}$ is the molar absorbance of FeH$_n$PO$_4^{n+}$, and Fe$_T$ is given by

$$(\mathrm{Fe}_T) = (\mathrm{Fe}^{3+}) + (\mathrm{FeOH}^{2+}) + (\mathrm{FeH}_n\mathrm{PO}_4^{n+}) \tag{6}$$

Combining Equations (3) to (6) the equilibrium constant of reaction(1) can be expressed as follows

$$Q_n = \frac{(A - A_0)(H^+)^{3-n}[1 + Q_H/(H^+)]}{(A_1 - A)(H_3PO_4)}$$

or (7)

$$A = A_1 - \frac{[(1 + Q_H)/(H^+)](H^+)^{3-n}(A - A_0)}{Q_n(H_3PO_4)}$$

Thus a plot of A versus $(A - A_0)/(H_3PO_4)$ should give a straight line for a series of solutions which have varying concentrations of H_3PO_4 but have the same formal concentration of ferric iron (Fe_T) and hydrogen ions provided that within the concentration relations studied, $FeH_nPO_4^{n}$ is the only important phosphato complex species present. A_1 and $Q_n/(H^+)^{3-n}$ can be evaluated from the intercept and slope of such a plot. In order to obtain the equilibrium concentration of H_3PO_4 required by Equation (7) a series of approximations was made. First, Equation (7) was plotted by using H_3PO_4 concentrations as calculated from the total formal concentration of phosphate added P_T, by means of the equation $(H_3PO_4) = P_T/[1 + K_{H_3PO_4}/(H^+)]$, which were uncorrected for the amount of phosphate in the complex. An approximate value for A_1 and K was thus obtained. This was used to calculate the concentration of the complex and to provide improved values for the (H_3PO_4). The data were then replotted using these improved values. Usually not more than three approximations were necessary.

Fig. 2 shows a few representative examples of plots of Equation (7) for various series of solutions each series representing solutions of constant (H^+). The points are fitted by a straight line satisfactorily over rather wide H_3PO_4 concentrations.

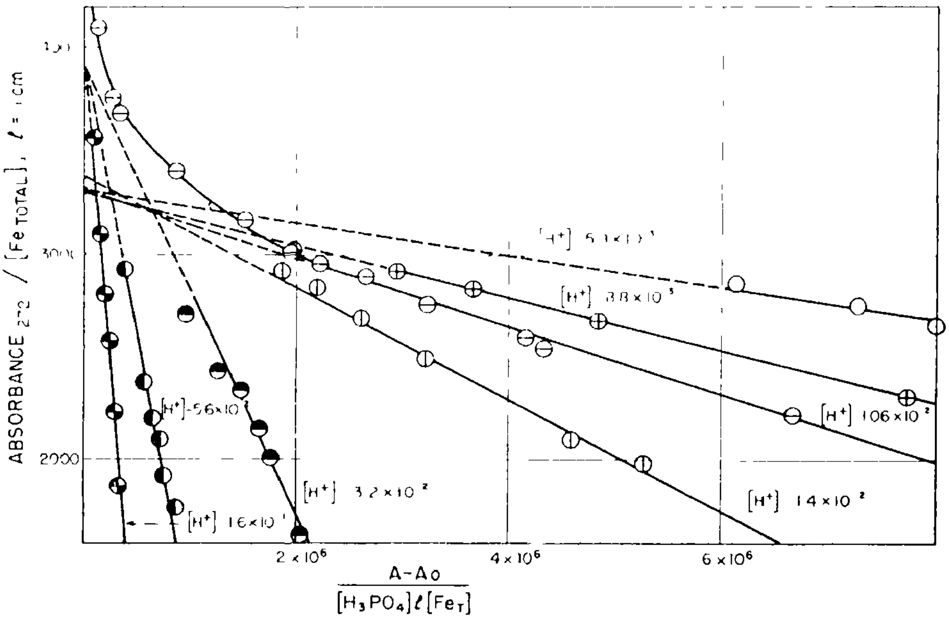


FIG. 2.—Plot of equation (7)

Fe_T^{III} in different experimental runs varied between 8 × 10^{-6} M and 5 × 10^{-5} M

However, points with a relatively high phosphate concentration (as indicated in Fig. 2 for the solutions having a $(H^+) = 2.06 \times 10^{-2}$) are above the straight line. This curvature is probably due to the formation of higher complex of the type $Fe(H_nPO_4)_x$. Attempts were made to fit such data in the higher phosphate concentration range assuming the formation of a diphosphato complex. However, no reliable information could be obtained concerning the second complex. The results displayed in Fig. 2 have been obtained with solutions containing total iron (III) concentrations of between 8×10^{-6} M and 5×10^{-5} M. Inconsistent results were obtained when ferric solutions more concentrated than 5×10^{-5} M were used. This is probably attributable to the formation of polynuclear complexes.

ANALYSIS OF REDOX POTENTIAL DATA

The concentration potential, E, observed between phosphate-free solutions of Fe(II) Fe(III) and corresponding phosphate containing solutions of equal (H^+), (Fe_t^{II}) and (Fe_t^{III}) is given by

$$E = -0.0592 \ln \frac{(Fe^{3+})(Fe_t^{II})}{(Fe^{2+})(Fe_t^{III})} \tag{8}$$

From Equations (1) and (8) and from stoicheiometric considerations the relationship[11]

$$[1 + Q_{11}/(H^+)]\,[\exp(E/0.0592) - 1] = Q_n(H_3PO_4)/(H^+)^{3-n} \tag{9}$$

can be derived.

This equation assumes that complex formation of phosphate with ferrous iron is negligible. (H_3PO_4) can be computed by successive approximations in the same way as described for the spectrophotometric data. According to Equation (9) a plot of the left hand term vs. (H_3PO_4) gives, for any set of data at constant (H^+), a straight line with a slope of $Q_n/(H^+)^{3-n}$. At high phosphate concentrations, deviations from a straight line were observed, thus indicating the formation of higher phosphato complexes.

Higher and polynuclear complexes. In order to obtain consistent values for $Q_n/(H^+)^{3-n}$ the total ferric iron concentration had to be kept below 5×10^{-5} M. At higher (Fe-III) computed Q_n values became progressively larger with increasing (Fe-III), thus giving evidence for the formation of polynuclear complexes. The data have been tested for some of the simplest assumptions, such as formation of $[Fe_2(H_nPO_4)_2]^{+2n}$ or $[Fe_2(H_nPO_4)]^{n+3}$. However, no reliable information on the types of polynuclear species formed was obtainable.

STABILITY OF $FeH_2PO_4^{2+}$ AND $FeHPO_4^+$

Fig. 3 represents a logarithmic plot of the spectrophotometric and potentiometric data according to Equation (1) in the form of

$$\log (FeH_nPO_4^{+n})/[(Fe^{3+})(H_3PO_4)] = \log Q_n - (3 - n) \log (H^+) \tag{10}$$

thus permitting the evaluation of n and Q_n from the slope and intercept. The ordinate values in Fig. 3, obtained from absorbance measurements, were computed from the plots in Fig. 2, dividing the slope by $[1 + Q_{11}/(H^+)]$. Values of $Q_n/(H^+)^{3-n}$ resulting from redox potential measurements are also plotted in Fig. 3. Reasonable agreement between these two sets of results is observed. It is evident from the logarithmic plot

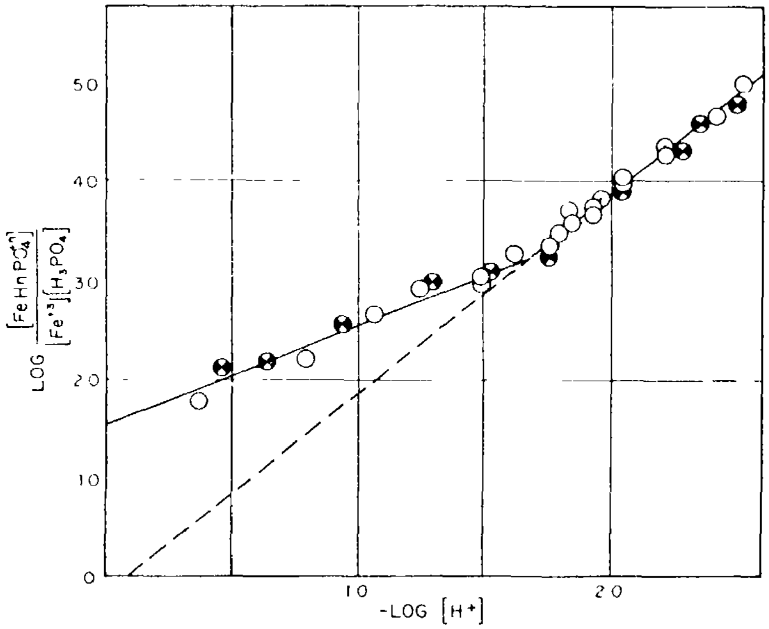


Fig. 3. Plot of equation (10).
○ Spectrophotometric data.
(⧗) Potentiometric data.

that there is a transition at log $[H^+] = 1.7$ where the slope of the fitted line changes from a slope of +1 to a slope of +2. From this we conclude that equilibrium (1) can be represented by the following expressions:

At $(H^+) < 2 \times 10^{-2}$ M

$$Fe^{3+} + H_3PO_4 = FeHPO_4^+ + 2H^+, \quad Q_1 \tag{11}$$

At $(H^+) > 2 \times 10^{-2}$ M

$$Fe^{3+} + H_3PO_4 = FeH_2PO_4^{2+} + H^+, \quad Q_2 \tag{12}$$

Table 1 summarizes the stability quotients obtained by the two different techniques. The results reported here are not in accord with the results reported by Lanford and Kiehl.$^{(2)}$ These authors used SCN^- for the determination of free Fe^{3+}. They interpreted their findings in terms of reaction (11) and reported a Q_1 of 15.5 at $\mu = 0.665$ and at 30°C. They found no evidence for the formation of $FeH_2PO_4^+$ although their solutions had (H^+) larger than 10^{-2} M. Their experiments were made in a Fe(III)

Table 1.—Stability quotients for $FeHPO_4^+$ and $FeH_2PO_4^{2+}$
(25 C, μ = 0.4)

	From e.m.f. measurement	From absorbance date
$Q_1 = (FeHPO_4^+)(H^+)^2/(Fe^{3+})(H_3PO_4)$	0.52	0.72
$Q_2 = (FeH_2PO_4^{2+})(H^+)/(Fe^{3+})(H_3PO_4)$	40	36
$K_1 = Q_1/(K_{H_3PO_4} K_{H_2PO_4^-}) = Fe(HPO_4^+)/(Fe^{3+})(HPO_4^{2-})$	1.7×10^8	2.3×10^8
$K_2 = Q_2/K_{H_3PO_4} = (FeH_2PO_4^{2+})/(Fe^{3+})(H_2PO_4^-)$	3.1×10^3	2.8×10^3

concentration range, where we find evidence for the formation of polynuclear phosphato-ferric complexes. It also appears possible that their solutions contained mixed thiocyanato phosphato complexes.

$FeH_2PO_4^{2+}$ has an acidity constant, $-\log K = 1{\cdot}7$, which is of the same order of magnitude as the first acidity constant of H_3PO_4. This value might be compared with a value of $-\log K = 2{\cdot}1$ proposed by BJERRUM and DAHM(15) for $AlH_2PO_4^{2+}$.

SOLUBILITY OF IRON (III) PHOSPHATE

It is apparent from the foregoing discussion that the solubility relations of $FePO_4$ are complicated by the formation of soluble phosphato-ferric complexes. Fig. 4 shows alkalimetric titration curves of $Fe(ClO_4)_3$, (2×10^{-3} M), of H_3PO_4, (2×10^{-3} M) and of an equimolar mixture of Fe(III) and H_3PO_4. It is evident from the titration curves that the addition of equimolar H_3PO_4 to the Fe(III) leads to a deprotonation of H_3PO_4 and does not result in an appreciable increase of base required to reach the equivalence point. This indicates that the reaction

$$Fe^{3+} + H_3PO_4 + 3OH^- = FePO_4 + 3H_2O \tag{13}$$

takes place predominantly. At pH values above 4, equilibrium is attained very slowly, the measured pH values drift, and the color of the precipitate changes from white to yellow, thus indicating the introduction of OH ions into the structure of the precipitate. COLE and JACKSON(7) have presented similar titration curves. Their evidence for regarding the tertiary phosphate as a dihydroxy-dihydrogen phosphate, however, does not appear to be conclusive.

In order to estimate a concentration solubility product, iron phosphate was precipitated from solutions containing $Fe(ClO_4)_3$, a small stoicheiometric excess of NaH_2PO_4, and 0·4 M $NaClO_4$. The solutions were adjusted to various H concentrations with $HClO_4$. Concentration conditions were selected so as to prevent formation

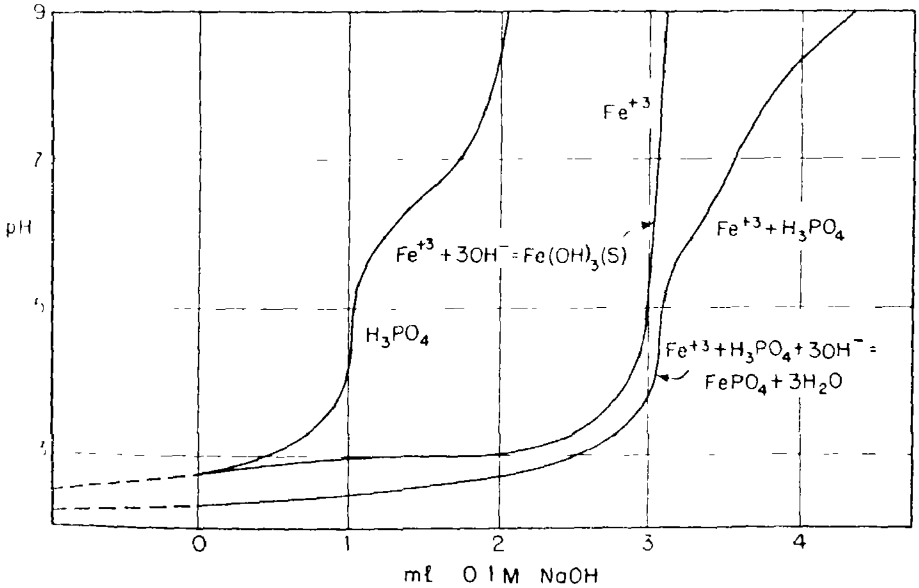


FIG. 4.—Alkalimetric titration of a 2×10^{-3} M $Fe(ClO_4)_3$ solution and of a 2×10^{-3} M H_3PO_4 solution and of an equimolar Fe^{3+}–H_3PO_4 mixture.

[15] BJERRUM and C. R. DAHM, *Z. Phys. Chem.*, Bodenstein-Festband, 627 (1931).

of higher and polynuclear complexes. Each solution was allowed to stand for at least three days. The solutions were then centrifuged or filtered through a membrane filter. Precipitates obtained within the pH range 1.5–2.6 were white and showed upon analysis a Fe to P ratio of unity. In aliquots of the supernatant or filtrate determinations of total iron and phosphate were made. Free (Fe^{3+}) was determined from e.m.f. measurements by the ferro-ferri method. Free (Fe^{3+}) was also calculated from total Fe(III) and total phosphate by assuming that the only soluble iron species are Fe^{3+}, $FeHPO_4^+$ and $FeOH^{2+}$. The values for (Fe^{3+}) calculated by this method were 5–20 times larger than the values obtained from e.m.f. measurements in the solutions. It can be inferred from this observation that it is difficult to separate from the solution the solid iron phosphate which has a tendency to be present in colloidal form. Thus it is not surprising that the described experimental procedure did not give particularly constant values for the solubility product of iron (III) phosphate. Using $10^{-20.7}$ for the product of the three acidity constants of H_3PO_4, values obtained for the solubility product at 25°C, $Q_s = (Fe^{3+})(PO_4^{3-})$ vary between $10^{-22.8}$ and $10^{-21.6}$. These values are somewhat lower than the value of 10^{-22} reported by ZHAROVSKII(9). The operational value of such a solubility product is somewhat limited unless the various complex formation equilibria between iron (III) and phosphate have been elucidated.

Acknowledgement—This work supported by the U.S. Public Health Service Research Grant WP13

J. Inorg. Nucl. Chem. 1963, Vol. 25, pp. 575 to 580. Pergamon Press Ltd. Printed in Northern Ireland

THE STATE OF MOLYBDENUM (VI) IN PERCHLORIC ACID SOLUTIONS

M. L. FREEDMAN
Refractory Metals Laboratory, General Electric Company, Cleveland 17, Ohio

(*Received* 30 *April* 1962, *in revised form* 18 *October* 1962)

Abstract—Solubility measurements of molybdic oxide and of the molybdic oxide hydrates were made to determine the nature of the ionic species formed in 0–6 N perchloric acid solutions. Both hydrates produce the same molybdic acid in water and the same monovalent cation in 0.1–1.0 N perchloric acid. Each hydrate forms its own unique molybdic acid in perchloric acid more concentrated than 2 N. Solubility equilibrium was not observed for molybdic oxide which produced different ions than the hydrates.

MOLYBDIC acid in the free state, in contrast to the isopolymolybdates which exist only as salts, is known only in solution. Graham first prepared molybdic acid solutions by reacting barium molybdate with sulphuric acid and MURGIER further developed this method to obtain stable solutions.[1] Richardson used an ion exchange method instead and observed that a colourless "glass" was formed on evaporating the molybdic acid solution.[2] DOUCET determined the constitution of Graham's molybdic acid, which he found identical with $MoO_3 \cdot 2H_2O$ solution, by exhaustive cryometric and conductometric studies.[3] The solute species consist of polymers of the monomeric tetramolybdic acid, $H_2Mo_4O_{13}$. Since this tetramolybdic acid is not related to the tetramolybdate salts, $M_4Mo_8O_{26}$, the name "Graham's molybdic acid" will be retained here for clarity.

While Graham's acid is the only well characterized molybdic acid it cannot be obtained in crystalline form. On the other hand, MoO_3, $MoO_3 \cdot H_2O$ and $MoO_3 \cdot 2H_2O$ each crystallizes from acidified molybdate solutions under various conditions.[4] These are formally acid anhydrides. Since their crystal structures are different each solid might possibly form its own unique polynuclear acid in solutions where it was the stable crystal form. There is some evidence that these compounds do produce different dissolved species. Thus, $MoO_3 \cdot 2H_2O$ has been reported to produce a HMo_2O_6 cation in perchloric acid[5] while MoO_3 produces other cationic species in this solvent.[6] Also, aqueous solutions freshly prepared from $MoO_3 \cdot H_2O$ and from $MoO_3 \cdot 2H_2O$ appear to contain different ions. The $MoO_3 \cdot H_2O$ solution is stable at 100°C while the solution made from $MoO_3 \cdot 2H_2O$ precipitates MoO_3 on boiling.

The solubilities of MoO_3, $MoO_3 \cdot H_2O$, and $MoO_3 \cdot 2H_2O$ were measured at 25°C in 0–6 N perchloric acid to determine their ranges of stability and the nature of the dissolved species formed by each compound. Since $MoO_3 \cdot 2H_2O$ spontaneously recrystallizes as $MoO_3 \cdot H_2O$ at 50°C, the solubility of only the latter compound was measured at 50°C. Equilibrium solubility measurements identify the stable solid phases of lowest solubility. Also since the activity of the solid is constant, the solubility curve is characteristic only of the dissolved ions, as shown by JONES for MoO_3.[6] Thus, if an anion is formed the logarithmic solubility curve will have a negative slope equal to the average number of protons generated by the formation of each anion. The concentration solubility product constant is written in terms of S, the solubility in moles of MoO_3 per litre, and Z, the polymerization number of the anion.

---

[1] M. MURGIER, *C. R. Acad. Sci., Paris* **208**, 583 (1939).
[2] E. RICHARDSON, *J. Inorg. Nucl. Chem.* **9**, 267 (1959).
[3] Y. DOUCET and S. BUGNON, *J. Chem. Phys.* **54**, 155 (1957).
[4] M. L. FREEDMAN, *J. Amer. Chem. Soc.* **81**, 3834 (1959).
[5] F. CHAUVEAU, R. SCHAAL and P. SOUCHAY, *C. R. Acad. Sci., Paris* **240**, 194 (1955).
[6] M. M. JONES, *J. Amer. Chem. Soc.* **76**, 4233 (1954).

$$\text{Solid} \rightleftharpoons \text{Anion}^{n-} + n\text{H}^+$$

$$K = (1/Z)S(H^+)^n \qquad \text{Hence, } d(\log S)/d(\log H^+) = -n$$

Conversely, if a cation is formed the slope will be positive and equal to the average number of protons bound per cation.

$$\text{Solid} + nH^+ \rightleftharpoons \text{Cation}^{n+}$$

Activity coefficients for the unknown ions must be ignored, and ionic strength cannot be kept constant by adding neutral salts since these may react with the hydrates. The observed solubilities will therefore tend to rise with increased perchloric acid concentration. Also the solubility measurements cannot give any information about polymerization numbers. However, since the solubilities of the three compounds will be measured in the same solutions, a direct comparison can be made of the dissolved species.

Perchloric acid was used as the solvent since it is the only strong acid which is not known to form complex ions with Mo(VI). Complexes with nitric acid have been reported[7] while those with hydrochloric and sulphuric acids are well known.[5] Solubility data for the hydrates in perchloric acid have not been reported while the data for MoO_3 covers only a small range of acid concentrations.[6]

EXPERIMENTAL

The two hydrates were prepared free from alkali by previously described methods.[1] Reagent grade MoO_3 was further purified by sublimation and the sublimed crystals were ground to fine powder in an agate mortar. Reagent grade perchloric acid was diluted to obtain stock solutions of approximately 6.1 and 0.1 N. These were standardized by titration with sodium hydroxide solution and then diluted as calculated to obtain other acid concentrations.

Solubility determinations were made in 30 ml polyethylene bottles which contained 1 g of sample and 20 ml of solution. These were sealed with Neoprene stoppers and inserted into a perforated plastic disc which was rotated at 1 rev/min in a thermostatted water bath. Portions of solutions were taken for analysis at 2 week intervals, a 1 ml pipette capped with filter paper being used to withdraw the sample. Molybdenum was determined as the thiocyanate complex using a Beckman DU spectrophotometer. Equilibration was continued until constant values were obtained. The dihydrate showed little change after the first two weeks although the run was continued for six weeks. The same values were obtained with the dihydrate when equilibrium was approached from the reverse direction, by saturating at 35° and then equilibrating for two weeks at 25°C. Eight weeks were used for the monohydrate, and the oxide equilibration was continued for eighteen weeks.

The dissolved Mo(VI) contributes substantially to the acidity below 0.1 N perchloric acid so the acidity of these solutions was measured with a Beckman G pH meter at the conclusion of the runs. The solid residues were also examined to determine whether phase changes had taken place during the long equilibration periods. The residues were recovered by filtration and dried at room temperature after washing with water. Analyses were made for combined water by ignition at 500°C and these showed little change from initial values Examination of a number of residues by X-ray diffraction confirmed that phase changes had not taken place The residues were unchanged in appearance except that crystal growth of the monohydrate had taken place in the strongly acid solutions

---

[7] P. H. COOPE and W. P. THISTLETHWAITE, *J. Inorg. Nucl. Chem.* 2, 125 (1956).

Experiments were also made to determine the rate at which phase changes took place by recrystallization when both phases were present A mixture of equal weights of MoO_3 $2H_2O$ and MoO_3 H_2O was completely converted to MoO_3 H_2O after two weeks of equilibration in 4 N perchloric acid at 25 C, as shown by X-ray diffraction The reverse change took place in 2 N perchloric acid Mixtures of the two hydrates were unchanged after four weeks in water and in 1 N perchloric acid at room temperature However, crystal growth of the hydrates from water solution was shown as follows An excess of MoO_3 $2H_2O$ was stirred for a few minutes in boiling water, and the solution was then rapidly filtered and cooled The solution contained 0 15 mole per litre of MoO_3, more than ten times the equilibrium value A portion of the solution formed a brittle, glassy gel on evaporation at room temperature The concentration of the solution was reduced to 0 02 mole per litre by equilibration with MoO_3 $2H_2O$ for a week at room temperature and to 0 03 mole per litre when MoO_3 H_2O was used

Mixtures of MoO_3 with MoO_3 $2H_2O$ in 2 N perchloric acid and with MoO_3 H_2O in 4 N perchloric acid were unchanged after four weeks at 25 C Solubility measurements were also made at 25 C with mixtures of equal weights of MoO_3 and MoO_3 $2H_2O$ The solubilities of the mixtures equaled the sum of the separate solubilities below 2 N acidity, after two weeks of equilibration The solubilities at higher acid concentrations were only slightly higher than those of MoO_3 $2H_2O$ alone

RESULTS

Solubility curves for the two hydrates are shown in Fig 1 while the apparent solubility of MoO_3 is shown in Fig 2 The perchloric acid strength at concentrations greater than 0 1 N was arbitrarily calculated as the product of the mean molar

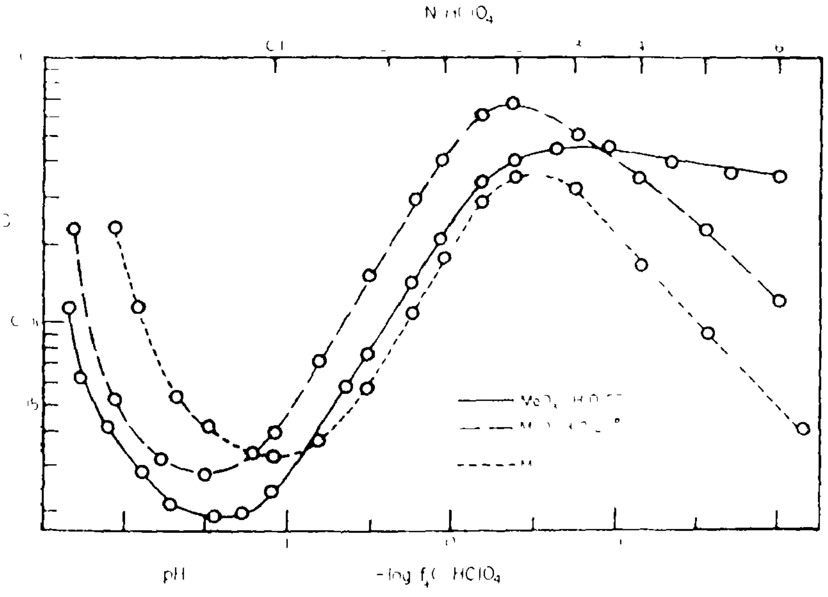


Fig 1 Solubility of molybdic oxide hydrates in perchloric acid

activity coefficient and concentration Molar activity coefficients were calculated from available molal coefficients [9] Figure 1 shows that MoO_3 $2H_2O$ is the stable

---

[8] G Chauveau, *C R Acad Sci, Paris* **242**, 2154 (1956)

[9] R A Robinson and R H Stokes *Electrolytic Solutions* p 476 Academic Press New York (1955)

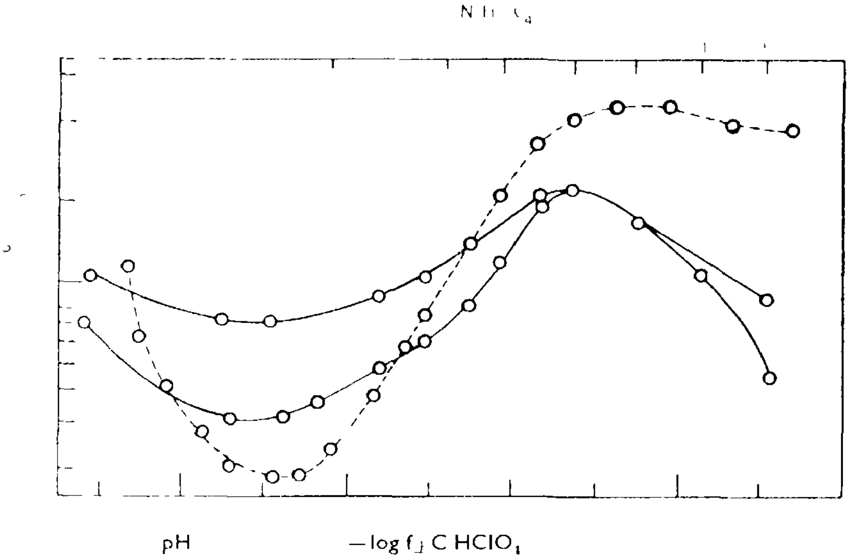


Fig. 2. Solubility of molybdic oxide in perchloric acid at 25°C.
Upper curve, eighteen weeks; lower curve, two weeks; dashed curve, $MoO_3 \cdot 2H_2O$.

solid phase at 25°C in perchloric acid concentrations lower than 3.5 N while $MoO_3 \cdot H_2O$ is the stable phase at higher acid concentrations. Both hydrates have similar solubility curves in the 0–2 N perchloric acid range. The solubility curves of $MoO_3 \cdot H_2O$ at 25°C and at 50°C are also very similar.

The negative slope of the $MoO_3 \cdot 2H_2O$ solubility curve at pH 2 shows that an anion is formed in solution. The limiting slope of −2 observed at the highest pH value is consistent with the formation of Graham's acid as previously reported for such solutions. At the 0.01 mole per litre of MoO_3 level, the dissolved species have been reported to consist of 50% $H_2Mo_4O_{13}$ monomer and a series of higher polymeric acids, $H_2Mo_8O_{25}$, $H_2Mo_{12}O_{37}$, etc.(3) These moderately strong acids generate two protons per anion regardless of the polymerization number. As the perchloric acid concentration is increased the solubility decreases to a minimum at the 1.5 pH isoelectric point. From a pH of 1 to a perchloric acid concentration of 1 N the slope of +1.0 is then consistent with the formation of the $HMo_2O_6^+$ cation of CHAUVEAU.(8) A solubility product constant of $1.23 \pm 0.03 \times 10^{-2}$ is calculated for $MoO_3 \cdot 2H_2O$ in this range of perchloric acid concentrations. The solubility reaches a maximum at the second isoelectric point in 3 N perchloric acid. The slope of −0.12 at higher perchloric acid concentrations shows that a new anion is present. This new molybdic acid, designated "Acid A", may have a high polymerization number or a low degree of ionization to account for the small slope.

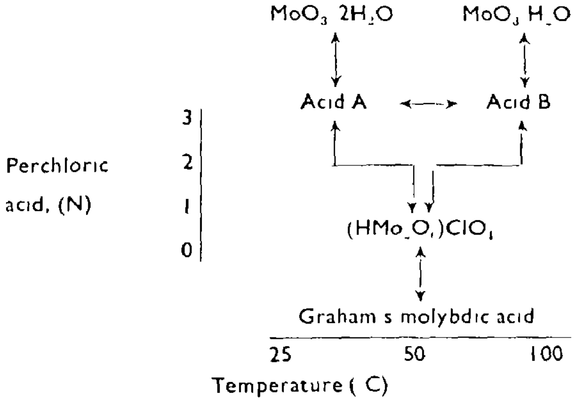
The solubility curves of $MoO_3 \cdot H_2O$ have a maximum in 2 N perchloric acid at both 25° and 50°C. At lower perchloric acid concentration $MoO_3 \cdot H_2O$ is apparently in equilibrium with the same dissolved species as $MoO_3 \cdot 2H_2O$. However, an anion species unique to $MoO_3 \cdot H_2O$ is present in the 2–6 N perchloric acid range. This second new molybdic acid is designated "Acid B". The observed slope of −0.65 suggests a stronger acid of lower polymerization number than "Acid A".

The apparent solubility of MoO_3 after two and eighteen weeks of equilibration is compared with that of $MoO_3 \cdot 2H_2O$ in Fig. 2. The continuous change in apparent solubility with time shows that equilibrium was not reached The solubility values after two weeks are slightly lower than those reported by JONES[(6)] but rise to higher values in eighteen weeks MoO_3 is apparently metastable with respect to MoO_3 $2H_2O$ in dilute perchloric acid, but there was no indication of an equilibrium between the compounds over the times involved Also, both hydrates appear to be metastable with respect to MoO_3 at perchloric acid concentrations greater than 2 N, but this conversion also was not observed

DISCUSSION

The molybdic acids "A" and "B" whose existence in solution is deduced from the solubility curves are to be distinguished from various "γ-" and "β-molybdic acids" reported in the old literature,[(10)] Heating MoO_3 $2H_2O$ in water, or preferably dilute acid, at 50°C results in recrystallization to MoO_3 H_2O, Rosenheim's "γ-molybdic acid" MoO_3 precipitates instead at 100 C in water so that MoO_3 is one of Rosenheim's "β-molybdic acids" A second "β-molybdic acid" was deduced from an inflection at 60°C in the solubility curve of MoO_3 H_2O in water However, X-ray diffraction shows that MoO_3 H_2O crystallized at 25 C is identical with MoO_3 H_2O obtained from solution at 100 C The inflexion in the solubility curve observed by Rosenheim was thus due to the fact that MoO_3 H_2O is not the stable solid phase at the lower temperatures in water A second, yellow MoO_3 H_2O is obtained only as an unstable intermediate in the solid state dehydration of MoO_3 $2H_2O$[1]

The relationship of the hydrates to dissolved species as a function of perchloric acid concentration and temperature is summarized as follows



The structure of "Acid A" should be related to that of MoO_3 $2H_2O$, and the structure of "Acid B", if polynuclear, should be related to that of MoO_3 H_2O However nothing is known regarding structures of the dissolved species or of MoO_3 H_2O The slow rate of equilibration of the hydrates with dilute perchloric acid solutions is apparently due to the low concentrations of "Acid A" and "Acid B" in such solutions CHAUVEAU, from her spectrophotometric measurements, considered the HMo_2O_6 ion as the predominant species to a perchloric acid concentration of 5 N[(8)] The bility measurements show new anion species to be formed above 2 N This apparent disagreement suggests that "Acid A" solutions may have optical properties similar to those of the cation salt solutions. The electrolytic transport and ion exchange experiments of BABKO and NABIVANETS[(11)] also show that Mo(VI) is present as an anion in solution of pH 1, and as a cation when the pH $\leq$ 1. However, from their transport experiments, these investigators considered the cation to be monomeric MoO_2^{2+} or $MoO(OH)_2^{2+}$. This conclusion is in disagreement with that of CHAUVEAU and with the findings of the present investigation.

---

[1] melin's *Handbuch der Anorganischen Chemie, Molybdan*, Vol 53, p 109 Verlag Chemie, Berlin 935)

Acknowledgement—The author thanks F. J. MILLER, JR. for assistance with some of the solubility determinations.

(11) A. K. BABKO, B. I. NABIVANETS, *Chem. Abstr.* **52**, 13382 (1958).

J. Inorg. Nucl. Chem. 1963, Vol. 25, pp. 581 to 594. Pergamon Press Ltd. Printed in Northern Ireland

SOME ASPECTS OF SYNERGISM IN SOLVENT EXTRACTION*—I

URANIUM (VI)

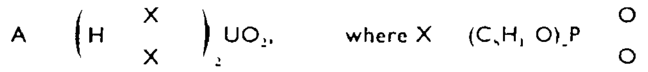
M. ZANGEN†

Abstract—Synergistic extraction of U(VI) from 0.3 N HCl was studied, using combinations of a monoacidic phosphate or phosphonate ester (the chelating agent) with a neutral organophosphorus compound (the synergist) at varying concentrations in benzene or cyclohexane.

A correlation was found between the acid strength of the chelating agent and its performance in synergistic extraction.

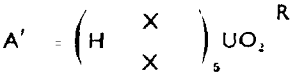
From the antisynergistic slope and the concentration of neutral synergist yielding the maximum distribution ratio, the formula of the extracted species and the constants governing the extraction equilibrium are derived.

IN studying the extraction of U(VI) from dilute sulphate solutions into a kerosene solution of di(2-ethylhexyl)phosphoric acid, BAES *et al.*[1] found a substantial increase in the distribution ratio on addition of small quantities of neutral organophosphoric compounds which, used alone under the conditions of the experiment, would hardly extract any U(VI) at all. This synergistic effect, being much stronger than e.g. the case reported by GOBLE and MADDOCK[2], had to be explained in terms of formation of specific, more extractable complexes. On the basis of the model suggested by BAES *et al.*[3] for the chelate complex of U(VI) with di(2-ethylhexyl)phosphoric acid dimer,



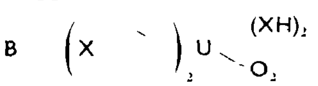
$$A = \left(H \begin{smallmatrix} X \\ \\ X \end{smallmatrix}\right)_2 UO_2, \qquad \text{where } X = (C_8H_{17}O)_2P \begin{smallmatrix} O \\ \\ O \end{smallmatrix}$$

in which uranium has the co-ordination number six, BLAKE *et al.*[1] suggested that with participation of the neutral additive R the extracted species is



$$A' = \left(H \begin{smallmatrix} X \\ \\ X \end{smallmatrix}\right)_5 UO_2^{\;R}$$

where uranium has the co-ordination number seven. The synergism in this case would then be analogous to the phenomenon found in the extraction of U(VI) with TTA.[5,6] However, KENNEDY suggested the model



$$B = \left(X\right)_2 U \begin{smallmatrix} (XH)_2 \\ \\ O_2 \end{smallmatrix}$$

---

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

† Israel Atomic Energy Commission Laboratories, Rehovot, Israel, at the time of this work Affiliate of the International Institute of Nuclear Science and Engineering, Argonne National Laboratory, Argonne, Illinois.

(1) C. A. BLAKE, C. F. BAES JR., K. B. BROWN, C. F. COLEMAN and J. C. WHITE, *Proceedings of the Second International Conference on Peaceful uses of Atomic Energy, Geneva* 15 P 1550 United Nations (1958).

(2) A. G. GOBLE and A. G. MADDOCK, *Trans. Faraday Soc.* **55**, 591 (1959).

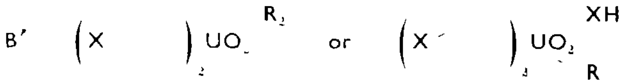
(3) C. F. BAES JR., R. A. ZINGARO and C. F. COLEMAN, *J. Phys. Chem.* **62**, 129 (1958).

(4) C. A. BLAKE, D. E. HORNER and J. M. SCHMITT, U.S.A.E.C. Report ORNL-2259 (1959).

(5) H. IRVING and D. N. EDGINGTON, *J. Inorg. Nucl. Chem.* **15**, 158 (1960).

(6) T. V. HEALY, *J. Inorg. Nucl. Chem.* **19**, 314 (1961).

with co-ordination number eight without synergist and



$$B' \quad (X \qquad)_2UO_2\,R_2 \quad \text{or} \quad (X^- \qquad)_3UO_2\,{}^{XH}_{R}$$

when one or both of the co-ordinated monomers of chelating agent are replaced by synergist molecules Support for this model was found by the adsorption of the chelate on phosphonate resin,[8] which took place by liberation of two HX- monomers per U

Later a new model was proposed by KENNEDY and DEANE[9] on the basis of infra-red spectra These authors suggest

$$C \quad \left[(X \qquad)_3UO_2\right] \quad HXH^+$$

as the species extracted in the absence of synergist and

$$C' \quad \left[(X \qquad)_3UO_2\right] \quad RH$$

when the neutral compound participates In both models B and C , therefore, the synergist substitutes for HX, although we might also conceive addition in the latter case, viz

$$C'' \quad \left[(X \qquad)_3UO_2\right] \quad RHXH^+$$

DYRSSEN and KUČA[10], studying the synergistic extraction of U(VI) from sulphate solutions by mixtures of dibutylphosphate and tributylphosphate in carbon tetrachloride, show that synergism is based on a substitution mechanism However, their calculations are based on the effective concentrations of HX and R, which were calculated on the assumption that the complex RHX (and no other) is formed This is also contended by HARDY and SCARGILL[11], but BAKER and BAES[12] and DYRSSEN and LIEM[13] suppose the complex to be $R(HX)_2$ for which the latter even propose a tentative structure

The present work was aimed at extending the knowledge about the synergistic effect to other acidic phosphate and phosphonate esters when combined with the neutral synergists di(2-ethylhexyl)2-ethylhexylphosphonate, dibutylbutylphosphonate and trioctylphosphine oxide A pure diluent, either benzene or cyclohexane, was preferred to kerosene, a mixture with undefined and variable composition Also, with the exception of a few experiments made for comparison, a hydrochloric rather than sulphuric aqueous phase was used, whereby the interference by aqueous complexation of U(VI) was reduced (Complexation by chloride is much weaker than by sulphate, and unlike in the $HSO_4^- \leftrightarrow SO_4^{2-}$ system, independent of the pH)

---

[7] J KENNEDY, AERE C/M-369 (1958)

[8] J KENNEDY, E A BURFORD and P G SAMMES, *J Inorg Nucl Chem* **14**, 114 (1960)

[9] J KENNEDY and A M DEANE, *J Inorg Nucl Chem* **19**, 142 (1961)

[10] D DYRSSEN and L KUČA, *Acta Chem Scand* **14**, 1945 (1960)

[11] C J HARDY and D SCARGILL, *J Inorg Nucl Chem* **11**, 128 (1959)

[12] H T BAKER and C F BAES JR , U S A E C Report ORNL-CF-58-5-93 (1958)

[13] D DYRSSEN and D H LIEM, *Acta Chem Scand* **14**, 1091 (1960)

EXPERIMENTAL

Sources of materials

The neutral synergists. Di(2-ethylhexyl)2-ethylhexylphosphonate (henceforth DEH[EHP]) and dibutylbutylphosphonate (DB[BP]) were obtained from Virginia-Carolina Chemical Co., trioctylphosphine oxide (TOPO) from Eastman Organic Chemicals.

All were further purified as follows:

(1) Stirring a 1 : 4 solution in benzene with an equal volume of 6 M HCl for 8 hr (to hydrolyse any pyrophosphate present).

(2) Washing out the HCl with two equal volume portions of water.

(3) Stirring with an equal volume of 1 M Na_2CO_3 for 15 min (to neutralize any acidic phosphate or phosphonate).

(4) Washing out the Na- salts with three equal volume portions of water.

(5) Evaporating any dissolved water and any alcohol possibly formed by hydrolysis in steps 1 or 3 under reduced pressure.

(6) The freedom of the neutral synergist from acidic contaminants was checked by a series of U(VI) extractions by the synergist alone from varying aqueous HCl concentrations. The distribution ratio for synergist alone being proportional to $[Cl^-]^2$ hence to $[HCl]^2$, while the distribution ratio for the acidic chelating agent alone is proportional to $[H^+]^{-2}$, hence to $[HCl]^{-2}$ the deviation of the plot *D* vs. [HCl] (on a log–log scale) from a −2 slope indicates the content of acidic chela chelating agent. Whenever this was found higher than 10^{-4}, a new cycle of purification (1)–(5) was carried out.

The chelating agents. Di(2-ethylhexyl)phosphoric acid (HDEHP) and di para(1,1,3,3 tetramethylbutyl)phenyl phosphoric acid (HDOϕP) were separated from a mixture of mono- and diester obtained from Victor Chem. and purified as reported by PEPPARD *et al.*(11) 2-ethylhexylhydrogen chloromethylphosphonate (HEH[ClMP]) and paraphenylphenyl, hydrogen chloromethylphosphonate (Hϕ_2[ClMP]) were prepared by esterification of $CH_2ClPOCl_2$ with the corresponding alcohols and further purified by the same methods.(11) 2-ethylhexyl, hydrogen 2-ethylhexylphosphonate (HEH[EHP]) was prepared by hydrolysis of DEH[EHP] and purified as reported by PEPPARD *et al.*(12)

The purity of all acidic chelating agents from neutral contaminants (as neutral esters, alcohols) was ascertained by titration of known aliquots.

The ^{233}U tracer was from Argonne National Laboratory stocks, purified by liquid extraction methods.

The distribution ratios were determined by the radiometric method.(11)

RESULTS

(a) *Extraction by varying concentrations of* DEH[EHP], DB[BP] *and* TOPO *in benzene or cyclohexane* (*in the absence of acidic chelating agent*), *from* 0.3 M HCl. This was done in order to be able to correct synergism results for the extraction due to the synergist alone. Results are shown in Fig. 1.

(b) *Extraction by* 0.01 F HEH[EHP] + *varying concentrations of* DEH[EHP] *in benzene or cyclohexane from* 0.3 N HCl *or* 0.3 N H_2SO_4. Figure 2 shows almost no synergistic (nor antisynergistic) effects, except for a slight maximum in the system cyclohexane–hydrochloric acid.

(c) *Extraction by* 0.01 F HDEHP + *varying concentrations of* DEH[EHP] *in benzene or cyclohexane, from* 0.3 N HCl *or* 0.3 N H_2SO_4. Results are shown in Fig. 3. Since the plots obtained with H_2SO_4 are mainly similar to those obtained with HCl but displaced downward (this is probably due to stronger complexing of U(VI) in the aqueous phase), further experiments were conducted only in hydrochloric solutions. A maximum increase in D by a factor of ~10 for cyclohexane and of ~2.5 for benzene was found for 0.06 M and 0.1 M DEH[EHP] respectively.

---

(11) D. F. PEPPARD, G. W. MASON, J. L. MAIER and W. J. DRISCOLL, *J. Inorg. Nucl. Chem.* **4**, 334 (1957).

(12) D. F. PEPPARD, J. R. FERRARO and G. W. MASON, *J. Inorg. Nucl. Chem.* **12**, 60 (1959).

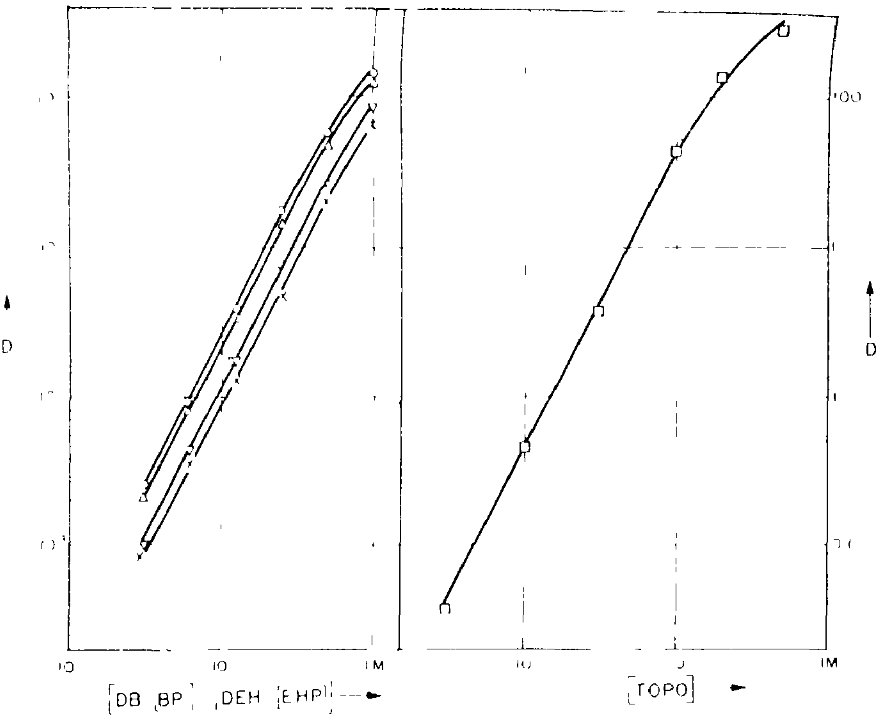


FIG. 1. Extraction of UO_2^{2+} from 0.3 N HCl by {
□ TOPO in cyclohexane
○ DB[BP] in cyclohexane
△ DEH[EHP] in cyclohexane
∇ DB[BP] in benzene
× DEH[EHP] in benzene

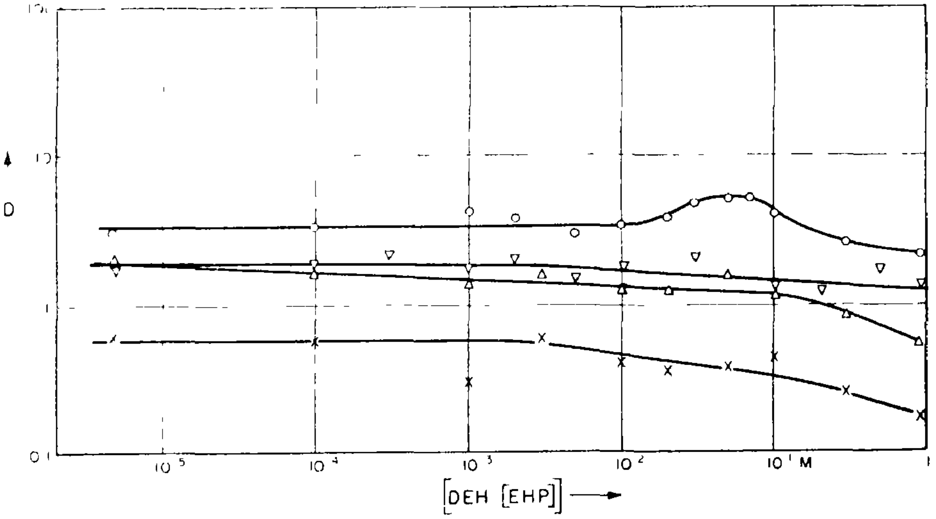


FIG. 2.—Extraction of UO_2 from {
0.3 N HCl by 10^{-1} F HEH[EHP] in {○ cyclohexane, ∇ benzene}
0.3 N H_2SO_4 by 10^{-1} F HEH[EHP] in {△ cyclohexane, / benzene}

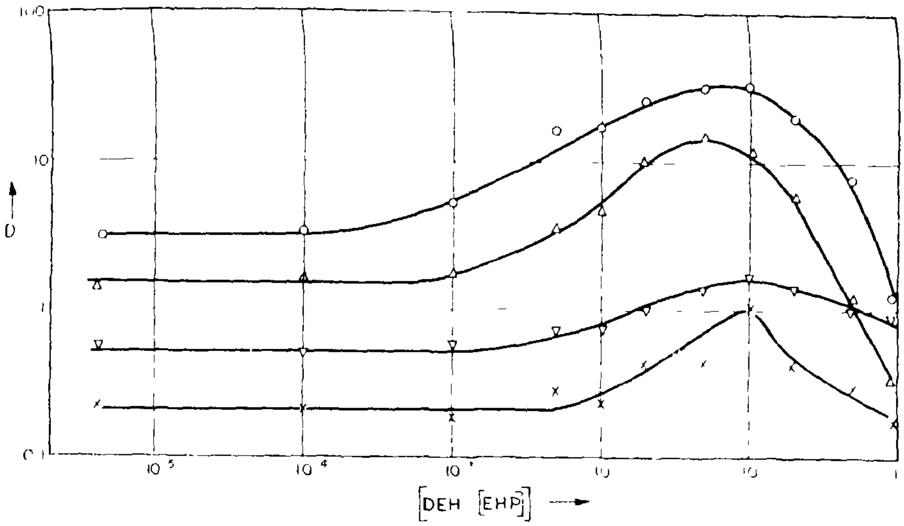


FIG. 3.—Extraction of UO_2^{2+} from $\begin{cases} 0.3\text{ N HCl by }10^{-2}\text{ F HDEHP in } \begin{cases} \circ \text{ cyclohexane} \\ \triangledown \text{ benzene} \end{cases} \\ 0.3\text{ N }H_2SO_4\text{ by }10^{-2}\text{ F HDEHP in } \begin{cases} \triangle \text{ cyclohexane} \\ \times \text{ benzene} \end{cases} \end{cases}$

(d) *Extraction by* 0.01 F HDOϕP + *varying concentrations of* DEH[EHP] *in benzene or cyclohexane from* 0.3 N HCl. Figure 4 shows a maximum increase in D by a factor of ~15 for cyclohexane and ~6 for benzene, at 0.007 M and 0.02 M DEH[EHP] respectively. In all systems considered till here, benzene as diluent appears to be unfavourable to synergism (a parallel observation was made by HEALY[16] in the extraction by TTA + neutral organophosphorus compound), use of benzene was therefore discontinued.

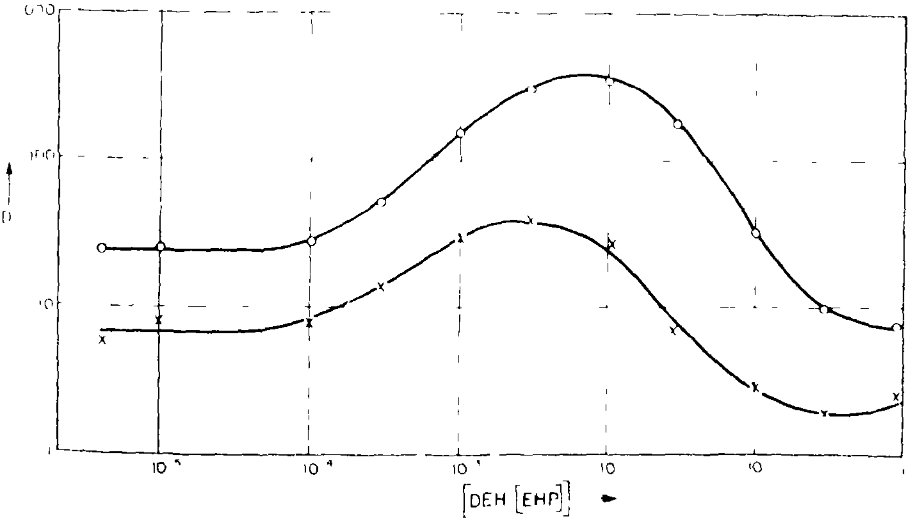


FIG. 4.—Extraction of UO_2^{2+} from 0.3N HCl by 10^{-2} HDOϕP in $\begin{cases} \circ \text{ cyclohexane} \\ \times \text{ benzene} \end{cases}$

---

[16] V. HEALY, *J. Inorg. Nucl. Chem.* **19**, 328 (1961).

(e) *Extraction by* 0 001 F HEH[EHP] *or* 0 001 F HDOφP : *varying concentrations of* DEH[EHP] *in cyclohexane from* 0 3 N HCl Results are shown in Fig 5 The synergistic effect was found to disappear for HEH[EHP] and to start at lower synergist concentrations for 10^{-3} F HDOφP than with ten times more concentrated chelating agent The maximum also occurred at lower synergist concentration, 0 003 M, while the factor of maximum increase in D was somewhat less (~12) The dotted curves show the results after correction for extraction by the synergist alone

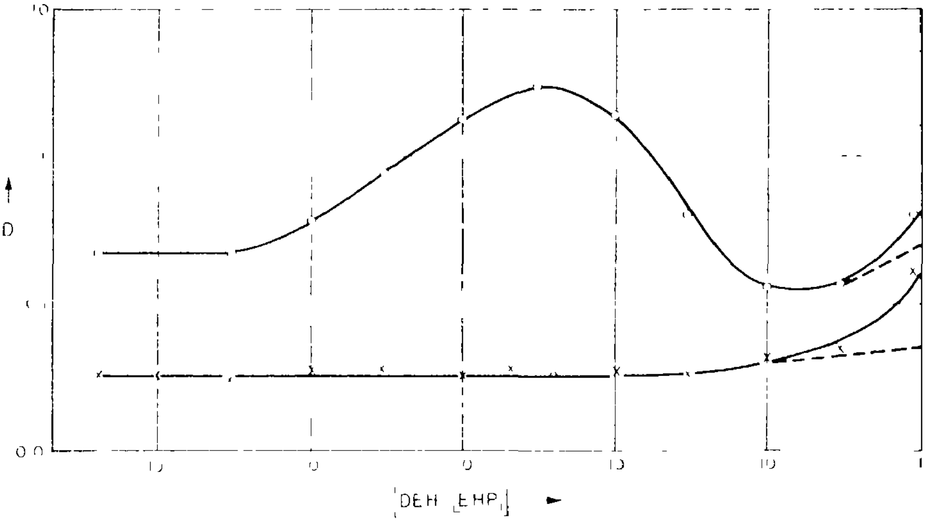


Fig. 5 Extraction of UO_2^{2+} from 0 3 N HCl by $\left\{\begin{array}{l} 10^{-3}\ \text{HDO}\varphi\text{P} \\ 10^{-3}\ \text{HEH[EHP]} \end{array}\right\}$ in cyclohexane

(f) *Extraction by* 0 001 F HDEHP *or* 0 001 F HEH[ClMP] , *varying concentrations of* DEH[EHP] *in cyclohexane from* 0 3 N HCl Results are shown in Fig 6

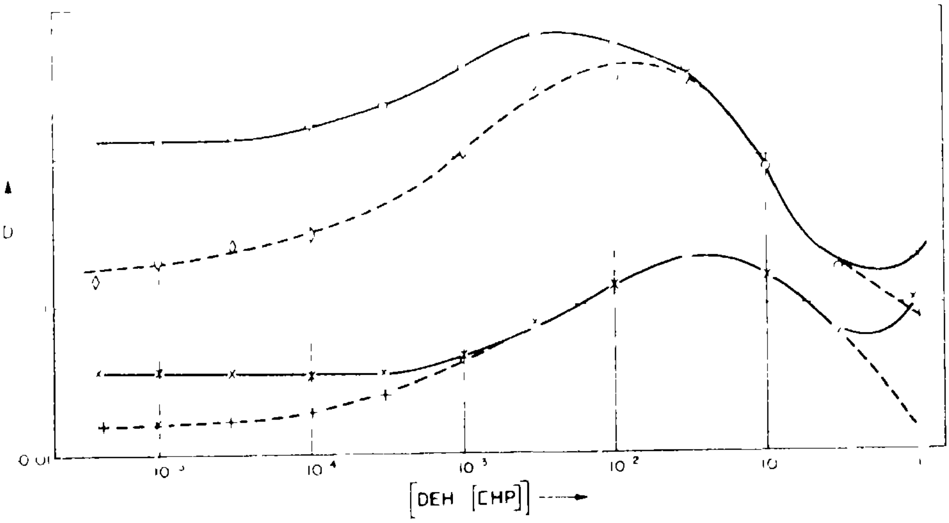


Fig. 6 – Extraction of UO_2^{2+} from 0 3 N HCl by

○ 10^{-3} F HEH[ClMP] in cyclohexane
- ○ with preequilibration
- , without preequilibration

× 10^{-3} F HDEHP in cyclohexane
- × with preequilibration
- + without preequilibration

Since at this low concentration these chelating agents report partly to the aqueous phase (where they exist as monomers), the distribution ratio would correspond to a lower effective concentration of chelating agent Therefore, the aqueous phase was preequilibrated several times with fresh organic phase, until saturation of the aqueous phase with chelating agent was shown by a constant value of D The number of necessary pre-equilibration stages decreased with increasing synergist concentration, also, the deviation of D_{obs} for a non-pre-equilibrated aqueous phase (shown by the dotted curves) from the correct values was higher at low concentrations of synergist Without pre-equilibration, therefore, the results would show a much stronger synergistic effect than actually exists A maximum increase in *D* by a factor of ~6 for HDEHP and of ~7 for HFH[ClMP] was found at 0 045 M and 0 004 M DEH[EHP] respectively

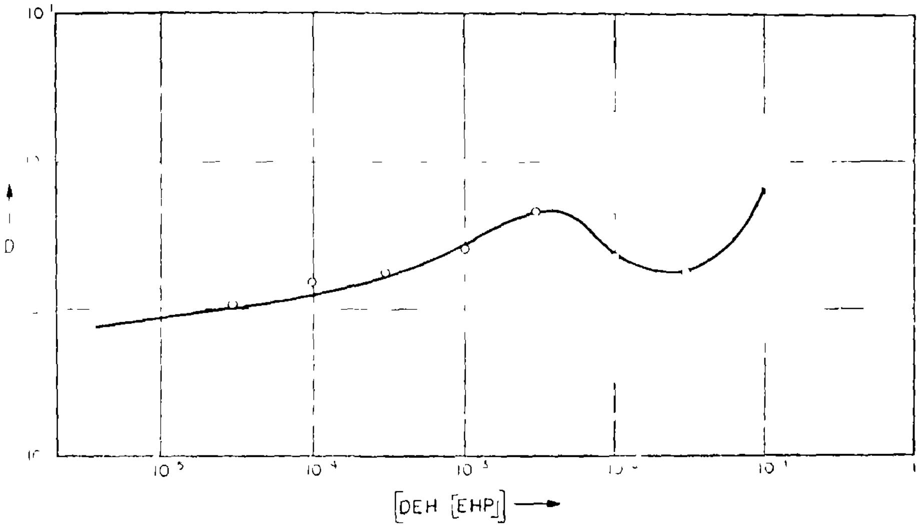


Fig 7 Extraction of UO_2^{2+} from 0 3 N HCl by 9 10 saturated Hqq [ClMP] in cyclohexane

(g) *Extraction by* 9/10 *saturated* Hqq [ClMP] *varying concentrations of* DEH [EHP] *in cyclohexane from* 0 3 N HCl Since the synergistic effect appears to increase with increasing acid strength of the chelating agent (see discussion below), it was expected to be very high in this case However, the solubility of Hqq [ClMP] in cyclohexane is so low (10^{-4} F) that very low distribution ratios were found therefore results here may be somewhat doubtful A maximum increase in *D* by a factor of ~6 was found for 0 003 M DEH[EHP] (Fig 7)

(h) *Extraction by* 0 01 F HEH[EHP], HDEHP *or* HDOqP *varying concentrations of* DB[BP] *in cyclohexane from* 0 3 N HCl Figure 8 shows maxima for the same concentrations of DB[BP] as found previously for DEH[EHP] but the maximum increase in *D* is higher, respectively ~2 ~13 and ~20 for HEH[EHP], HDEHP and HDOqP

(i) *Extraction by* 0 001 F HEH[EHP] *or* HDOqP *varying concentrations of* DB[BP] *in cyclohexane from* 0 3 N HCl Results are shown in Fig 9 Again the maximum for HDOqP occurs at the same concentration of DB[BP] as previously

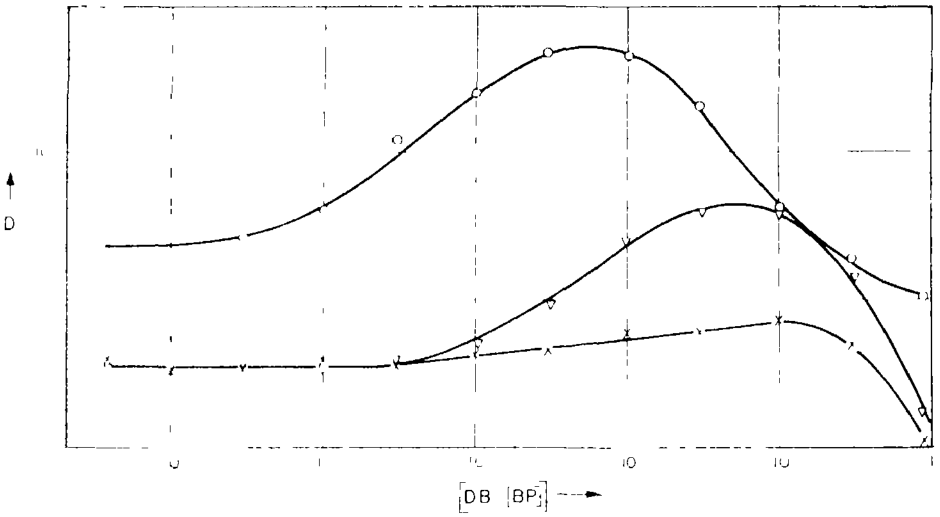


FIG 8 Extraction of UO_2^{2+} from 0 3 N HCl by 10^{-2} F {○ HDOφP; ▽ HDEHP; × HEH[EHP]} in cyclohexane

found for DEH[EHP], but it is higher (factor of ~16 instead of ~12) For HEH[EHP] a slight maximum is found at 0 05 M DB[BP], which however could be due to experimental error

(j) *Extraction by* 0 01 F HEH[EHP], HDEHP *or* HDOφP *varying concentrations of* TOPO *in cyclohexane from* 0 3 N HCl Results are shown in Fig 10 Maximum increase factors for *D* of respectively ~30, ~120 and ~140 were found at 0 013, 0 009 and 0 005 M TOPO respectively The dotted curves show the results after correction for extraction by the synergist alone No data can be obtained for higher than 0 45 M TOPO, which is near the limiting solubility in cyclohexane

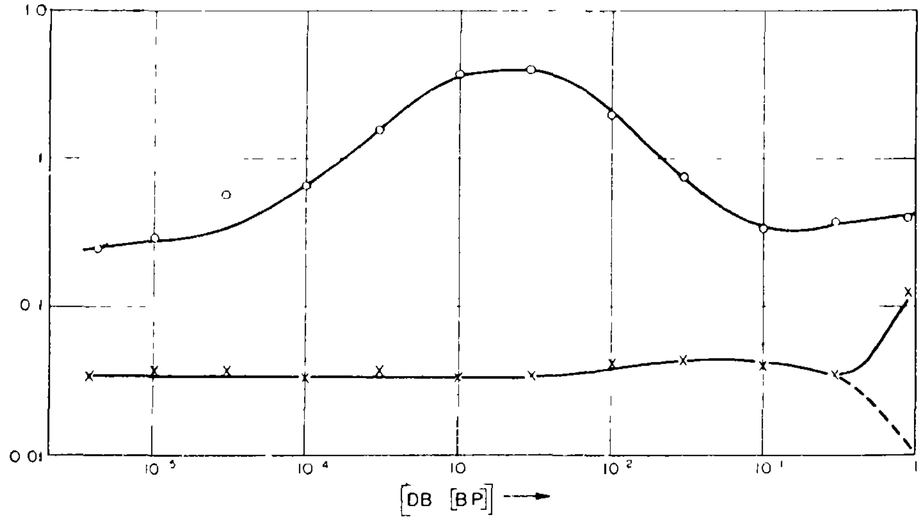


FIG 9 —Extraction of UO_2^{2+} from 0 3 N HCl by {○ 10^{-3} F HDOφP; × 10^{-3} F HEH[EHP]} in cyclohexane

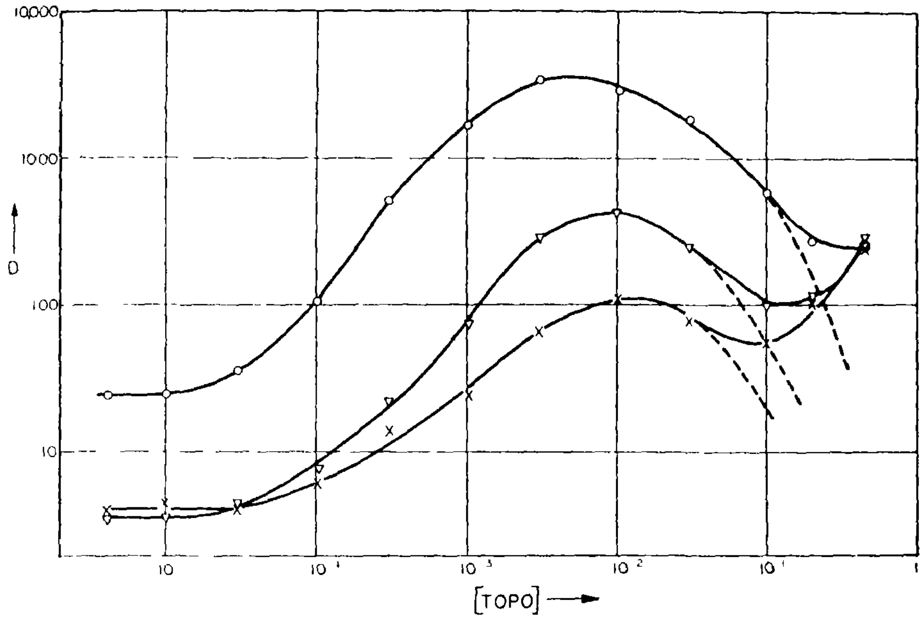


FIG. 10 Extraction of UO_2^{2+} from 0.3 N HCl by $\left\{\begin{array}{l}10^{-2}\text{ F HDO}\varphi\text{P}\\10^{-2}\text{ F HDEHP}\\10^{-2}\text{ F HEH[EHP]}\end{array}\right\}$ in cyclohexane

(k) *Extraction by* 0.001 F HDOφP + 0.003 M DB[BP] *in cyclohexane from varying concentrations of* HCl. Figure 11 shows an inverse second power dependency of *D* on $[H^+]$ over the whole range.

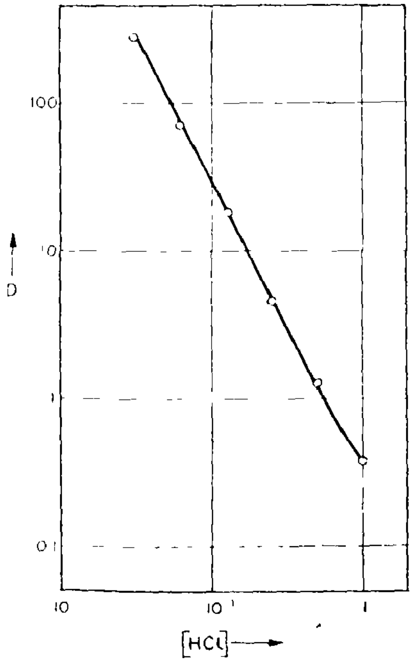


FIG. 11.—Extraction of UO_2^{2+} from HCl by 10^{-3} F HDOφP + 3 × 10^{-3} M DB[BP] in cyclohexane

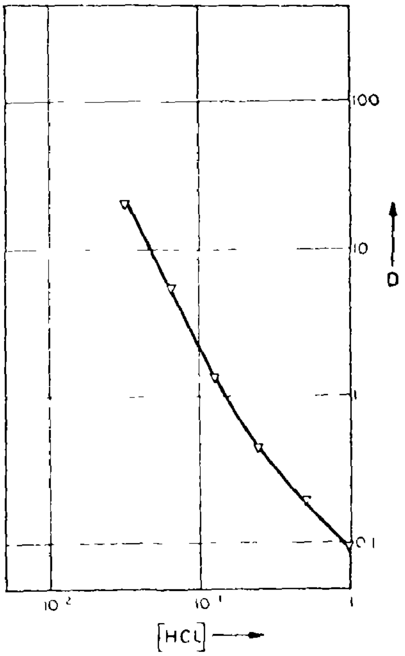


FIG. 12. Extraction of UO_2^{2+} from HCl by 10^{-3} F HDOφP + 0.3 M DB[BP] in cyclohexane

(l) *Extraction by* 0.001 F HDOφP + 0.3 M DB[BP] *in cyclohexane from varying concentrations of* HCl. Figure 12 shows the dependency of *D* on [HCl] to vary gradually from inverse second to inverse less-than-first power.

DISCUSSION

On the basis of the electronic structure of the various organic groups, the order of increasing acid strength for the chelating agents used in this work is expected to be HEH[EHP] HDEHP HEH[ClMP] HDOφP, which is identical with the order of increasing synergistic effect shown by the experimental results. It may seem surprising, in view of this correlation, that HEH[ClMP], which is expected to be a much stronger acid than HDEHP, should show almost identical synergistic behaviour. But then it may be asked also why, in the absence of synergist, HEH[ClMP] should extract U(VI) so much better than the other chelating agents. Possibly HEH[ClMP] could act as a tridentate ligand with participation of the chlorine and thereby form more stable complexes favouring extraction but resistant to synergistic effects. The relatively low synergistic effect obtained with Hφφ[ClMP] might be explained by the same hypothesis, in addition to the fact that synergism is lower when lower concentrations of chelating agent are used (compare Fig. 5 with Fig. 2 and 4).

This correlation between acid strength and tendency to synergistic extraction is in perfect agreement with model C above (although also to some extent with model B). The stronger the acid in other words the higher the partial positive charge on the POOH group, the more resistance to formation of the ion HXH^+ and the more improvement in extraction when HXH^+ is replaced by RH^+ (or by $HXHR^+$, as in model C'').

The decrease in *D* on further addition of synergist after the maximum *D* is attained is ascribed to complex formation between the synergist and the chelating agent.(3,4,6,9,10) However, as said above, there is disagreement whether this antisynergistic effect (the word should be antiergistic or antergistic, since "antisyn-" is a contradiction in terms) is due to formation of $(HX)_2R$ or of HXR. We have therefore to decide between four combinations of reactions:

$$\text{(a)}\quad UO_2{}^{2+}{}_{aq} + 2(HX)_{2\,or} + R_{or} \quad UO_2X_3^-\,HXHR^+_{or} \quad 2H^+_{aq}$$

$$(HX)_{2\,or} + R_{or} \quad (HX)_2R_{or}$$

with

$$K_a = \frac{[UO_2X_3^-\,HXHR^+]_{or}\,[H^+]_{aq}^2}{[UO_2^{2+}]_{aq}\,[(HX)_2]_{or}^2\,[R]_{or}} \tag{a-1}$$

or

$$K' = \frac{K_a}{[H^+]_{aq}^2} \quad \frac{D}{[(HX)_2]_{or}^2\,[R]_{or}} \tag{a-1'}$$

$$K = \frac{[(HX)_2R]}{[(HX)_2]\,[R]} \tag{a-2}$$

$$[(HX)_{2\,\text{total}}] = [(HX)_2]_{or} + 2[UO_2X_3^-\,HXHR^+] + [(HX)_2R] \tag{a-3}$$

and

$$[R_{\text{total}}] = [R] + [(HX)_2R] + [UO_2X_3^-\,HXHR^+] \tag{a-4}$$

$$(\mathrm{b})\ \mathrm{UO_2^{2+}}_{aq} + \tfrac{3}{2}(\mathrm{HX})_{2or} + \mathrm{R}_{or} \rightleftharpoons \mathrm{UO_2X_3^-{\cdot}HR^+}_{or} + 2\mathrm{H^+}_{aq}$$

$$(\mathrm{HX})_{2or} + \mathrm{R}_{or} \rightleftharpoons (\mathrm{HX})_2\mathrm{R}_{or}$$

with

$$K_u = \frac{[\mathrm{UO_2X_3^-\ HR^+}]_{or}\,[\mathrm{H^+}]_{aq}^2}{[\mathrm{UO_2^{2+}}]_{aq}\,[(\mathrm{HX})_2]^{3/2}_{or}\,[\mathrm{R}]_{or}} \qquad (b\text{-}1)$$

or

$$K' = \frac{K_u}{[\mathrm{H^+}]_{aq}^2} = \frac{D}{[(\mathrm{HX})_2]^{3/2}_{or}\,[\mathrm{R}]_{or}} \quad (b\text{-}1'), \qquad (b\text{-}2) = (a\text{-}2),$$

$$[(\mathrm{HX})_{2\,total}] = [(\mathrm{HX})_2]_{or} + \tfrac{3}{2}[\mathrm{UO_2X_3^-\ HR^+}] + [(\mathrm{HX})_2\mathrm{R}] \qquad (b\text{-}3)$$

and

$$[\mathrm{R}_{total}] = [\mathrm{R}] + [(\mathrm{HX})_2\mathrm{R}] + [\mathrm{UO_2X_3^-\ HR^+}] \qquad (b\text{-}4)$$

$$(\mathrm{c})\ \mathrm{UO^{2+}_{2\,aq}} + 2(\mathrm{HX})_{2or} + \mathrm{R}_{or} \rightleftharpoons \mathrm{UO_2X_3^-\ HXHR^+}_{or} + 2\mathrm{H^+}_{aq}$$

$$\tfrac{1}{2}(\mathrm{HX})_{2or} + \mathrm{R}_{or} \rightleftharpoons \mathrm{HXR}_{or}$$

with

$$(c\text{-}1) = (a\text{-}1)\quad (c\text{-}1') = (a\text{-}1'),\quad K = \frac{[\mathrm{HXR}]}{[(\mathrm{HX})_2]^{1/2}\,[\mathrm{R}]} \qquad (c\text{-}2),$$

$$[(\mathrm{HX})_{2\,total}] = [(\mathrm{HX})_2]_{or} + 2[\mathrm{UO_2X_3^-\ HXHR^+}]_{or} + \tfrac{1}{2}[\mathrm{HXR}] \qquad (c\text{-}3)$$

and

$$[\mathrm{R}_{total}] = [\mathrm{R}] + [\mathrm{HXR}] + [\mathrm{UO_2X_3^-\ HXHR^+}] \qquad (c\text{-}4)$$

$$(\mathrm{d})\ \mathrm{UO^{2+}_{2\,aq}} + \tfrac{3}{2}(\mathrm{HX})_{2or} + \mathrm{R}_{or} \rightleftharpoons \mathrm{UO_2X_3^-\ HR^+}_{or} + 2\mathrm{H^+}_{aq}$$

$$\tfrac{1}{2}(\mathrm{HX})_{2or} + \mathrm{R}_{or} \rightleftharpoons \mathrm{HXR}_{or}$$

with

$$(d\text{-}1) = (b\text{-}1),\qquad (d\text{-}1') = (b\text{-}1'),\qquad (d\text{-}2) = (c\text{-}2)$$

$$[(\mathrm{HX})_{2\,total}] = [(\mathrm{HX})_2]_{or} + \tfrac{3}{2}[\mathrm{UO_2X_3^-\ HR^+}]_{or} + \tfrac{1}{2}[\mathrm{HXR}] \qquad (d\text{-}3)$$

and

$$[\mathrm{R}_{total}] = [\mathrm{R}] + [\mathrm{HXR}] + [\mathrm{UO_2X_3^-{\cdot}HR^+}] \qquad (d\text{-}4)$$

In theory we could now, by combining each set of equations (1′), (2), (3) and (4), obtain an equation giving D as a function of $[\mathrm{R}_{total}]$ Comparing the obtained function with the experimental plots, the right mechanism could be determined and values assigned to the constants K and K' The calculations, however, become very involved and therefore the following simplified method is proposed

We first make the following assumptions

(1) The amounts of $(\mathrm{HX})_2$ and R bound in a complex with U(VI) are negligible with respect to any other species of $(\mathrm{HX})_2$ and R

(2) At the point of maximum synergism, D_{max}, the extent of U(VI) extraction not involving synergist is negligible with respect to the reaction governed by K'

It is then easy to eliminate all terms relating to species of R between the equations (1′), (2), (3) and (4), obtaining D as a function of $[(\mathrm{HX})_{2\,total}]$ and $[(\mathrm{HX})_2]_{or}$

Maximizing D with respect to $[(HX)_2]_{or}$ we then obtain the following expressions, valid for D maximum

for mechanism (a)
$$[(HX)_2]_{or\,max} = \tfrac{1}{2}[(HX)_{2\,total}]$$
$$[R_{total}]_{max} = \tfrac{1}{2}[(HX)_{2\,total}] + \frac{1}{K}$$
$$D_{max} = \frac{K'}{4K}[(HX)_{2\,total}]^2$$

for mechanism (b)
$$[(HX)_2]_{or\,max} = \tfrac{1}{3}[(HX)_{2\,total}]$$
$$[R_{total}]_{max} = \tfrac{2}{3}[(HX)_{2\,total}] + \frac{2}{K}$$
$$D_{max} = \frac{2K'}{3\sqrt{(3)}K}[(HX)_{2\,total}]^{3}$$

for mechanism (c)
$$[(HX)_2]_{or\,max} = \tfrac{2}{5}[(HX)_{2\,total}]$$
$$[R_{total}]_{max} = \tfrac{1}{5}[(HX)_{2\,total}] + \frac{4}{\sqrt{(15)}K}[(HX)_{2\,total}]^{1/2}$$
$$D_{max} = \frac{12\sqrt{(3)}K'}{25\sqrt{(5)}K}[(HX)_{2\,total}]$$

for mechanism (d)
$$[(HX)_2]_{or\,max} = \tfrac{1}{2}[(HX)_{2\,total}]$$
$$[R_{total}]_{max} = [(HX)_{2\,total}] + \frac{\sqrt{2}}{K}[(HX)_{2\,total}]^{1/2}$$
$$D_{max} = \frac{K'}{2K}[(HX)_{2\,total}]^2$$

These expressions can now be used to

(1) determine the mechanism by finding the dependency of D_{max} on the initial total concentration of chelating agent (there would however be no way to distinguish between (a) and (d))

(2) determine K from the total concentration of synergist that corresponds to the maximum distribution ratio

(3) determine K' and hence K_{ll} from K and the maximum distribution ratio

Another useful method is the elimination of $[(HX)_2]_{or}$ between the equations (1′) and (2), obtaining

$$(a\text{-}5)\quad D = \frac{K'[(HX)_2R]^2}{K^2[R]} \qquad (b\text{-}5)\quad D = \frac{K'[(HX)_2R]^3}{K^3[R]^2}$$

$$(c\text{-}5)\quad D = \frac{K'[HXR]^4}{K^4[R]^3} \qquad (d\text{-}5)\quad D = \frac{K'[HXR]^3}{K^3[R]^2}$$

If it is assumed that at a large excess of R over $(HX)_2$ the concentrations of any other species of the chelating agent are negligible with respect to the complex betwe chelating agent and synergist, the latter in turn being negligible with respect to the concentration of free synergist, we may write

$$[(HX)_2R] \approx [(HX)_{2\,total}] - \text{constant (for mech (a), (b))}$$

or

$$[HXR] \approx 2[(HX)_{2\,total}] \quad \text{constant (for mech (c), (d))}$$

and

$$[R] \approx [R_{total}]$$

At the limit of high synergist concentration the limiting slope of the plot D vs $[R_{total}]$ (on a log log scale) should be 1 for mechanism (a), ½ for (b), -3 for (c) and - 2 for (d), this makes it possible to determine the actual mechanism from the antisynergistic slope

Applying both methods, we can now rule out (1) mechanism (b) which requires a 3/2 power dependency of D_{max} on $[(HX)_{2\,total}]$ while the experimental results (comparing 0 01 F and 0 001 F HEH[EHP] HDEHP and HDOφP) show a power of 2 1 2 2 (2) mechanism (c), which requires an antisynergistic slope of −3, in disagreement with the experimental results (most slopes approximately −1 a few nearer 2) (3) mechanism (d), which requires $[R_{total}]_{max}$ $[(HX)_{2\,total}]$ in contradiction of the results observed with HDOφP

Having thus decided for mechanism (a) the following values are derived

for the system HEH[EHP] DEH[EHP] $K \sim 20$ $K' \sim 4$ 10^6
for the system HEH[EHP] DB[BP] $K \sim 20$ $K' \sim 5\ 5$ 10^6
for the system HEH[EHP] TOPO $K \sim 130$ $K' \sim 5\ 5$ 10^8
for the system HDEHP DEH[EHP] $K \sim 20$ $K' \sim 2\ 3$ 10^7
for the system HDEHP DB[BP] $K \sim 20$ $K' \sim 3\ 6$ 10^7
for the system HDEHP TOPO $K \sim 200$ $K' \sim 3\ 3$ 10^9
for the system HEH[ClMP] DEH[EHP] $K \sim 300$ $K \sim 7$ 10^9
for the system HDOφP-DEH[EHP] $K \sim 400$ $K' \sim 5$ 10^9
for the system HDOφP DB[BP] $K \sim 550$ $K' \sim 1$ 10^{10}
for the system HDOφP TOPO K and K' are too high to be determined by this method

It is obvious why, in the assumed mechanism the much more basic TOPO should be a better synergist The advantage of DB[BP] over DEH[EHP] however, remains unexplained A possible reason is the decrease in steric hindrance in the HXHR ion

At low chelating agent concentrations a minimum in D is observed at high concentration of synergist Correction of the results for extraction by the synergist alone still leaves in some cases a substantial increase in D after the minimum This may be explained with the assumption that the neutral extraction mechanism could take the form

$$UO^{2+}_{2\,aq} + (HX)_{2\,or} + Cl^-_{aq} \quad 2R_{or} \quad UO_2HX_2ClR_{2\,or} \quad H^+_{aq}$$

instead of

$$UO^{2+}_{2\,aq} + 2Cl^-_{aq} \quad 2R_{or} \quad UO_2Cl_2R_{2\,or} \qquad \text{(f)}$$

In order to ascertain whether there is any competition between extraction according to (a) and to (e), the dependency of D on $[HCl]_{aq}$ was studied at synergist concentrations corresponding to the top and the bottom of the antisynergistic slope Reaction

(a) should make D proportional to $[\mathrm{H}^+]_{\mathrm{aq}}^2$, hence to $[\mathrm{HCl}]^2$, while reaction (e) would make D proportional to $[\mathrm{Cl}^-]$ and to $[\mathrm{H}^+]^{-1}$, hence independent of [HCl]. Figures 11 and 12 show that there is no participation of (e) at $D_{\max}$, but that, at high [R], there is competition of both reactions, the part of (e) increasing with increasing [HCl].

Acknowledgement—The author wishes to thank the International Atomic Energy Agency, Vienna, and the Israel Atomic Energy Commission for grants which made this work at Argonne National Laboratory possible, D. F. PEPPARD and G. W. MASON, Argonne National Laboratory, for suggesting the problem, supplying the chelating agents, synergists and tracer and offering further valuable help and encouragement in the course of this work, and T. V. HEALY, for helpful discussion.

J. Inorg. Nucl. Chem. 1963. Vol. 25. pp. 595 to 600. Pergamon Press Ltd. Printed in Northern Ireland

EXTRACTION OF GROUP VIII METALS BY LONG CHAIN ALKYL AMINES—V

LIQUID ION-EXCHANGE BEHAVIOUR OF THE CYANIDE COMPLEXES OF IRON, COBALT AND NICKEL

S. E. Bryan, M. L. Good and G. J. Maus
Department of Chemistry, Louisiana State University, New Orleans

(*Received* 24 *September* 1962)

Abstract—The cyanide complexes of Fe(II), Fe(III), Co(III) and Ni(II) have been investigated with respect to their extractability by solutions of long chain alkyl amines in various solvents. The distribution of the anions, $Fe(CN)_6^{4-}$ and $Co(CN)_6^{3-}$ was determined by tracer methods using ^{59}Fe and ^{58}Co labelled potassium salts. For $Fe(CN)_6^{3-}$ and $Ni(CN)_4^{2-}$ spectrophotometric methods were used.

The results show the same trends as a previous study of the corresponding oxalate complexes, namely that the free base amines show virtually no extraction but good extraction is realized by using various salts of the amines. The cyanides are more readily extracted than their oxalate counterparts but the same ion-exchange behaviour is apparent.

PREVIOUS articles in this series report the extraction of the chloride, sulphate and oxalate complexes of the Fe, Co and Ni triad by long chain alkyl amines.[1-4] These studies have included specific investigations of the extraction mechanism and the nature of the extracted species in each system considered. To further define the extraction process of long chain alkyl amine–metal anion systems, a systematic study of the extraction of the cyanide complexes of Fe, Co and Ni was undertaken.

EXPERIMENTAL

Materials

A. *Preparation of complex cyanides*

1. $K_2Ni(CN)_4 \cdot H_2O$. This compound was prepared by a method reported by FERNELIUS and BURBAGE.[5] The orange crystals obtained were recrystallized from water and dried in a desiccator. Gravimetric analysis for nickel gave 22.6% Ni. Theoretical: 22.7% Ni.

2. $K_3Co(CN)_6$. This compound was prepared by a procedure reported by BIGELOW.[6] The compound was labelled with ^{58}Co by adding an aliquot of the isotope to the first step in the preparation. The resulting light yellow crystals were recrystallized from water and dried in a vacuum oven at 88°C. Analysis for Co was carried out by digesting a sample in concentrated H_2SO_4 and neutralizing the resulting solution with NaOH. The solution was then buffered to a pH of 7–8 and titrated with standard EDTA. Co content experimentally determined was 17.8%. Theoretical: 17.8% Co.

3. $K_3Fe(CN)_6$. This compound was not prepared. Baker's Analysed Reagent Grade material was used to make all solutions of this complex.

4. $K_4Fe(CN)_6$. This compound (labelled with ^{59}Fe) was prepared by adding a stoicheiometric amount of $FeCl_2$ (containing an aliquot of carrier-free ^{59}Fe as $FeCl_3$) dropwise to a solution of KCN. The resulting solution was heated until a yellow coloration was obtained. After cooling and filtering, the solution was evaporated until light yellow crystals began to form. The crystals were collected by filtration and dried in a desiccator. The solutions used experimentally were standardized by comparison to Beer's law curves made using Baker's Analyzed Reagent Grade material (see procedure below).

---

[1] M. L. GOOD and S. E. BRYAN, *J. Amer. Chem. Soc.* **82**, 5636 (1960).
[2] M. L. GOOD and S. E. BRYAN, *J. Inorg. Nucl. Chem.* **20**, 140 (1961).
[3] S. E. BRYAN and M. L. GOOD, *J. Inorg. Nucl. Chem.* **21**, 339 (1961).
[4] M. L. GOOD, S. E. BRYAN and F. JUGE, JR., *Inorg. Chem.* In press.
[5] W. C. FERNELIUS (Editor) *Inorganic Synthesis* Vol. 2, p. 227. McGraw-Hill, New York (1946).
[6] W. C. FERNELIUS (Editor), *Inorganic Synthesis* Vol. 2, p. 225. McGraw-Hill, New York (1946).

B. *Amines and other chemicals*

The amines used have been reported elsewhere$^{(1)}$ and all other materials were Analytical Reagent Grade.

Procedure

The procedure for obtaining the distribution of the two labelled complexes, $Co(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ has been previously described.$^{(3)}$ Spectrophotometric analysis was used to determine the distribution of the $Ni(CN)_4^{2-}$ and $Fe(CN)_6^{3-}$ complexes. Beer's law curves were determined for the Ni complex at its absorption maxima of 268, 284 and 308 mμ. By comparing the absorption values of these maxima before and after extraction, the percent Ni complex extracted could be determined. A similar procedure was used to determine the percentage extraction for $Fe(CN)_6^{3-}$ which has a strong absorption maximum at 420 mμ.

In studying the oxidation of $Fe(CN)_6^{4-}$ it was necessary to determine the amount of oxidation at various times, thus the spectra of this compound was determined and Beer's law curves were made for the absorption maximum at 316 mμ. Then by reading the absorption at 420 and 316 mμ the relative amounts of $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ in the solution could be determined.

All complete spectra were determined on a Beckman DK-1 spectrophotometer using 1 cm silica cells. Beer's law curves and concentration determinations made therefrom were obtained from absorbance measurements made on a Beckman DU spectrophotometer.

RESULTS AND DISCUSSION

The results of a general extraction study of three of the complex cyanides are given in Table 1. $Fe(CN)_6^{4-}$ is not included due to problems which will be discussed below. The free base amines extract negligible amounts of any of the complexes. However, pretreating the amines with acids to produce the amine salts increased the per cent extraction of all of the anions considered. Some trends can be readily ascertained from the data in Table 1. The primary amine salts are the most effective extractors for these anions, with the secondary amine and tertiary amine salts being poorer. This corresponds to a similar order obtained in the extraction of the corresponding oxalate complexes.$^{(3)}$ The solvent effect is pronounced only in the tertiary amines, where chloroform is a poorer solvent than benzene or toluene. This same effect was observed in the extraction of chlorocomplexes where tertiary amines are particularly good extractors.$^{(2)}$ Chloroform was superior in that its solutions showed less tendency to form emulsions. One interesting difference between these extractions and those for the corresponding oxalate complexes is the high per cent extraction of the dipositive Ni cyanide complex by all of the amines. This phenomena is probably due to the increased stability of the $Ni(CN)_4^{2-}$ as compared to $Ni(C_2O_4)_2^{2-}$. The tendency of the Ni complex to form solid precipitates when equilibrated with the amine salt solutions is striking. These solid materials have not been thoroughly investigated as yet but the colours associated with them are the same as that for the $Ni(CN)_4^{2-}$ indicating that this ion is not destroyed in the precipitation reaction.

The extractions carried out on the ferrocyanide complex were complicated by the oxidation of the ferrocyanide ion to ferricyanide in some of the systems studied. By doing spectrophotometric studies on the aqueous and organic phases of a given extraction it was possible to determine the extent of the oxidation at a particular time. The oxidation was very rapid for tertiary amine salts. As rapidly as the solutions could be analysed, some oxidation had occurred and the complete conversion of the ferrocyanide to ferricyanide in the extracted organic phase took place in a matter of minutes. A quarternary salt (tricapryl monomethyl ammonium chloride) was used as an extractant and it appeared as if the ferrocyanide was oxidized as it extracted into

TABLE 1 - PER CENT EXTRACTION OF $M(CN)_x^{y-}$ BY ALKYL AMINES

Amine[a] [b]	Solvent	$M(CN)_x^{y-}$	Free Base	Pretreating acid HNO$_3$	HClO$_4$	HCl	HAc	H$_2$SO$_4$
Primene 81-R	Benzene	$Co(CN)_6^{3-}$	0.0	[c]	90.4	[c]		[g]
		$Fe(CN)_6^{3-}$	0.0	87.5	90.1	93.1	94.5	[d]
		$Ni(CN)_4^{2-}$	6.1	—[e]	89.6	92.1	95.4	[g]
Primene 81-R	Toluene	$Co(CN)_6^{3-}$	0.0	88.5	91.5	[c]		—[e]
		$Fe(CN)_6^{3-}$	0.0	83.7	91.4	[c]	[c]	—[c]
		$Ni(CN)_4^{2-}$	0.0	—[e]	84.9	[c]	—	—[e]
Primene 81-R	Chloroform	$Co(CN)_6^{3-}$	0.0	85.4	94.8	75.8	99.0	97.9
		$Fe(CN)_6^{3-}$	10.1	88.7	88.1	80.7	98.0	98.5
		$Ni(CN)_4^{2-}$	—[e]	[e]	—[f]	—[e]	[e]	—[e]
2,2'-diethyl-dihexyl amine	Benzene	$Co(CN)_6^{3-}$	0.2	52.5	53.5	98.8	97.6	99.9
		$Fe(CN)_6^{3-}$	0.0	64.5	59.7	98.0	100.0	100.0
		$Ni(CN)_4^{2-}$	7.0	[c]	—[f]	—[f]	[g]	100.0
2,2'-diethyl-dihexyl amine	Toluene	$Co(CN)_6^{3-}$	0.0	66.1	[c]	99.3	97.3	100.0
		$Fe(CN)_6^{3-}$	1.5	59.0	—[f]	99.8	98.5	98.0
		$Ni(CN)_4^{2-}$	0.0	[f]	[f]	—[f]	[g]	100.0
2,2'-diethyl-dihexyl amine	Chloroform	$Co(CN)_6^{3-}$	0.0	31.0	60.4	98.6	99.7	99.9
		$Fe(CN)_6^{3-}$	0.0		69.5	98.5	99.3	100.0
		$Ni(CN)_4^{2-}$	4.8	99.3	99.8	100.0	99.9	100.0
tri-n-hexyl amine	Benzene	$Co(CN)_6^{3-}$	7.1	63.9	45.5	96.3	100.0	100.0
		$Fe(CN)_6^{3-}$	0.0	71.2	49.0	99.9	100.0	100.0
		$Ni(CN)_4^{2-}$	0.0	[f]	97.8	100.0	100.0	100.0
tri-n-hexyl amine	Toluene	$Co(CN)_6^{3-}$	0.5	59.7	47.8	81.7	96.5	99.1
		$Fe(CN)_6$	0.0	74.3	51.0	99.2	100.0	100.0
		$Ni(CN_4^{2-}$	2.3	[c]	100.0	[c]	100.0	100.0
tri-n-hexyl amine	Chloroform	$Co(CN)_6^{3-}$	0.5	28.8	26.5	97.9	98.4	99.8
		$Fe(CN)_6^{3-}$	4.8	37.3	43.2	99.2	99.8	100.0
		$Ni(CN)_4^{2-}$	00.0		—	[f]	100.0	100.0

[a] Amine conc. was 0.2 M

[b] Complex cyanide conc. was 0.01 M

Third layer formed

[d] Third layer formed with pretreating acid

Solid formed

Emulsion formed

Solid formed with pretreating acid

TABLE 2 PER CENT EXTRACTION OF $Fe(CN)_6^{4-}$ BY ALKYL AMINES

Amine*	Solvent	Free base	Pretreating acid HNO$_3$	HClO$_4$	HCl	HAc	H$_2$SO$_4$
Primene 81-R	Chloroform		77.7	95.1	93.4	99.0	81.5†
Tri n-hexyl amine	Chloroform	0.0	1.4	2.4	38.2	58.0	71.8
diethyl hexyl amine	Chloroform	0.2	9.4	20.4	73.6	93.0	99.5

Amine conc. is 0.1 M and $Fe(CN)_6^{4-}$ conc. is 0.01 M

Partial emulsion

the organic phase The oxidation reaction was much slower for the secondary amine salts and total conversion of the ferrocyanide in the organic phase did not occur for several hours The primary amine ferrocyanide solutions were stable with respect to oxidation for several hours Table 2 shows some of the extraction data obtained for the ferrocyanide ion All of this data was obtained by equilibrating the aqueous and organic phases for 3 min and immediately separating the layers Thus the per cent extraction of ferrocyanide (not ferricyanide) was determined The kinetics and mechanism of this oxidation reaction are presently being investigated in our laboratories

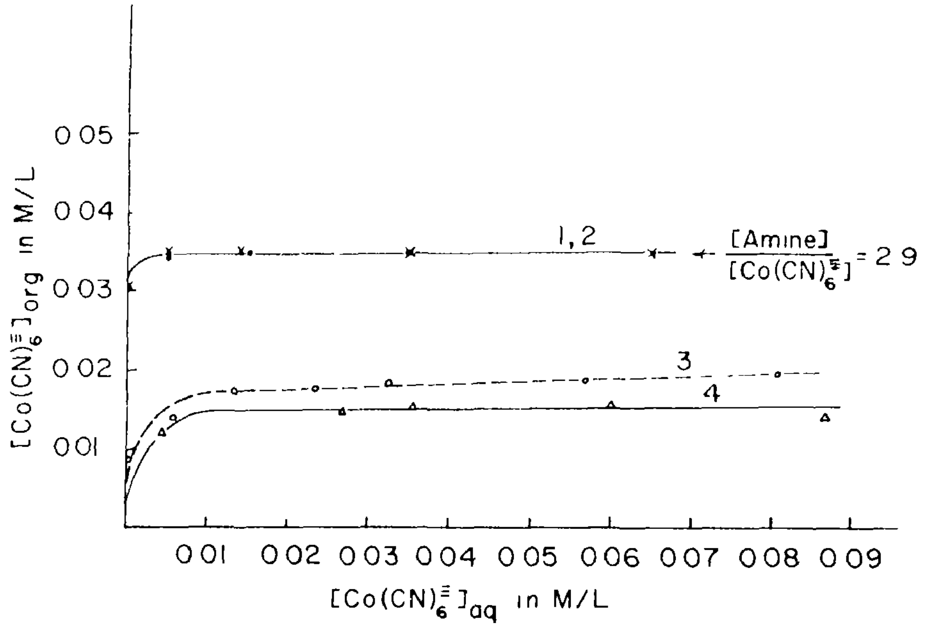


Fig 1 Extraction isotherms for $CO(CN)_6^{3}$ by amines in $CHCl_3$ Curve 1-H_2SO_4 pretreated tri-n-hexyl amine, Curve 2-H_2SO_4 pretreated 2 2′diethyldihexyl amine, Curve 3-HCl pretreated 2,2′diethyldihexyl amine, Curve 4-HCl pretreated tri-n-hexyl amine

In order to ascertain the extraction species involved in these studies, spectra of aqueous solutions of the complexes were compared to the spectra of the extracted species in the organic amine solutions In all cases the spectra for a given complex was the same before and after extraction indicating that the complex metal cyanide was extracted intact into the organic amine solution This would be compatible with an ion exchange mechanism for the extraction reaction Also the order of preference for the anions $ClO_4^- > NO_3^- > Cl^- > Ac^- > SO_4^{2-}$ is the same as that previously reported for the ion exchange resin studies [7] By comparing all of the extraction data presented in Tables 1 and 2 it can be seen that the extractability of the complex decreases as the charge on the ion increases This too is compatible with an ion-exchange extraction mechanism

Further elucidation of the extracting species was attempted by determining extraction isotherms for various extraction systems Representative curves are shown in Figs 1, 2, 3 and 4 The maximum loading of the amines occurs as predicted from

[7] R Bastian, *Analyt Chem* **23**, 580 (1951)

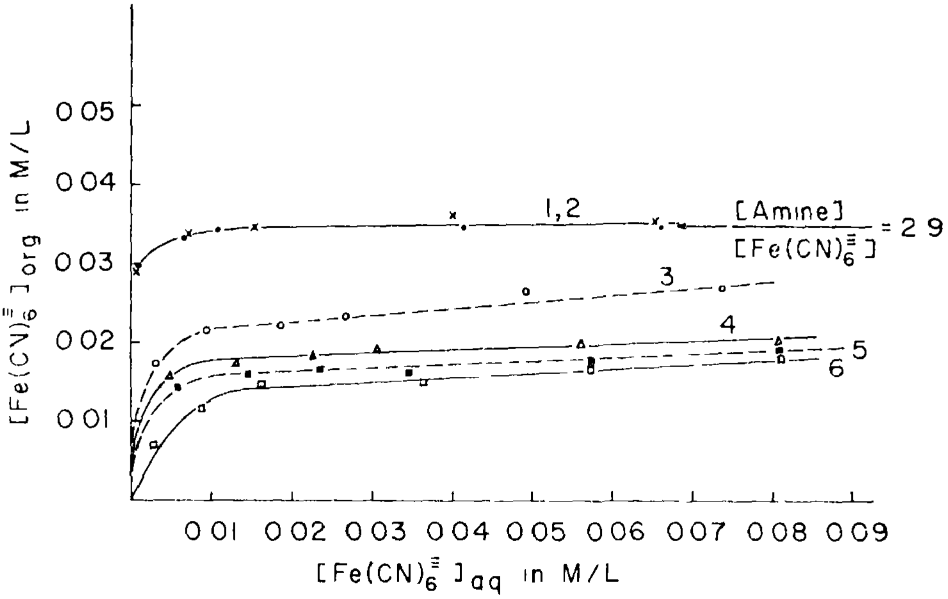


FIG. 2 —Extraction isotherms for $Fe(CN)_6^{4}$ by amines in $CHCl_3$ Curve 1-H_2SO_4 pretreated tri-n-hexyl amine, Curve 2-H_2SO_4 pretreated 2 2 diethyldihexyl amine Curve 3-H_2SO_4 pretreated Primene 81-R Curve 4 HCl pretreated 2 2′diethyldihexyl amine, Curve 5-HCl pretreated tri-n-hexyl amine, Curve 6-HCl pretreated Primene 81-R

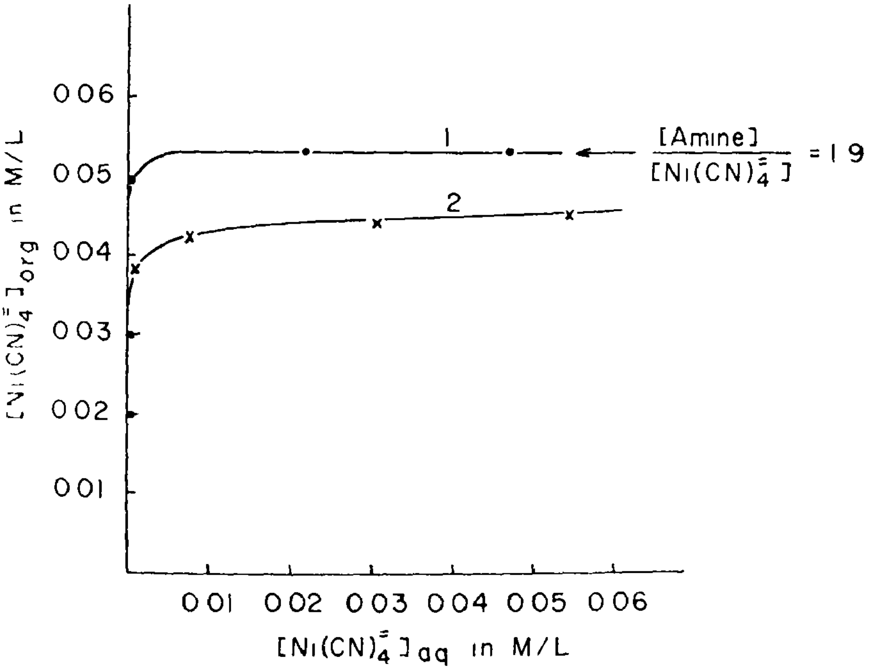


FIG. 3 —Extraction isotherms for $Ni(CN)_4^{2}$ by amines in $CHCl_3$ Curve 1-H_2SO_4 pretreated 2,2 diethyldihexyl amine Curve 2-HCl pretreated 2,2 diethyldihexyl amine

the charge on the complex ion: amine to metal ratio of three for $Co(CN)_6^{3-}$ and $Fe(CN)_6^{3-}$, two for $Ni(CN)_4^{2-}$ and four for $Fe(CN)_6^{4-}$. It is interesting to note however that *this maximum loading is realised only when the amine salt anion being* replaced is one which has a low affinity for the amine, namely sulphate or acetate. When chloride salts are involved the maximum loading is considerably below that predicted from the complex cyanide charge. This phenomena is also in keeping with the idea of an ion exchange reaction. Thus it appears that in all of the cases considered

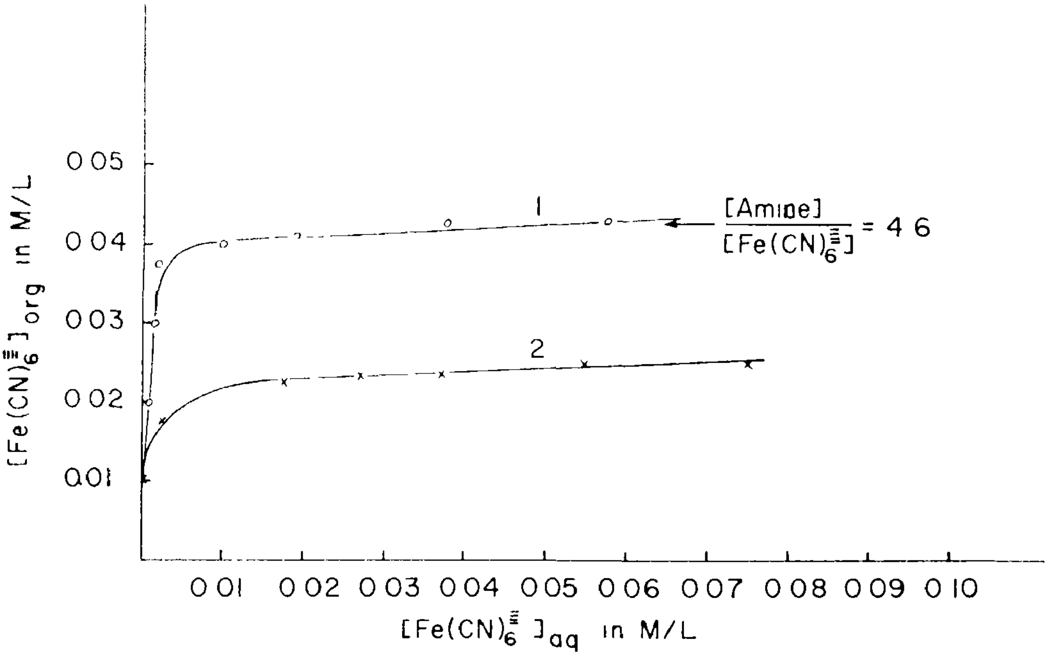


FIG. 4. Extraction isotherms for $Fe(CN)_6^{3-}$. Curve 1-HAc pretreated 2,2 diethyldihexyl amine in benzene. Curve 2-HCl pretreated Primene 81-R in $CHCl_3$.

in this study the extraction of the complex cyanides can be represented as follows

$$y[R_3NH^+]A^-_{(org)} + M(CN)_x{}^{y-}_{(aq)} \rightleftharpoons [R_3NH^+]_y[M(CN)_x]^{y-}_{(org)} + yA^-_{(aq)}$$

The extent of the reaction in the forward direction depends upon the relative concentrations of the reactants and the relative affinity of A^- and $M(CN)_x{}^{y-}$ for the amine cation.

A comparison of the data in Tables 1 and 2 with the extraction isotherms in Figs. 1–4 indicates the desirability of determining the extraction isotherms if the efficiency of an ion-exchange extraction is being considered. Although the differences between the extraction percentages for HCl and H_2SO_4 pretreats in the Tables are small, the loading capacities of the two pretreats are quite different. This derives from the fact that the data in the Tables is taken for situations where the amine salt is in considerable excess with respect to the complex being extracted.

Acknowledgements—We would like to thank the Rohm and Hass Company for their contributions of research quantities of some of the amines used.

The major part of this investigation has been supported by the United States Atomic Energy Commission under contract No. AT-(40-1)-2576.

J. Inorg. Nucl. Chem. 1963, Vol. 25, pp. 601 to 605. Pergamon Press Ltd. Printed in Northern Ireland

STABILITY OF A DILUTE SOLUTION OF SODIUM IN LIQUID AMMONIA

I. WARSHAWSKY*
Brandeis University, Waltham, Massachusetts

(*Received* 30 *July* 1962; *in revised form* 28 *August* 1962)

Abstract—It has been observed that hydrogen is evolved when sodium is distilled in a Pyrex system under "strict" vacuum conditions. Evidence is presented which suggests that the hydrogen evolution is due to a chemical reaction between the sodium and strongly adsorbed water on the surface of the Pyrex glass.

It is very difficult to prepare a dilute solution of sodium in liquid ammonia at -78°C without some decomposition. This work deals with an investigation of the source of this instability. Evidence has been obtained which suggests that the strongly adsorbed layer of moisture at the glass liquid interface is responsible for the decomposition. After this layer of moisture is effectively removed from the interface, the system appears to be stable at -78°C.

THERE is a paucity of quantitative data in the literature for dilute solutions of alkali metals in liquid ammonia. A possible explanation for this suggested by KRAUS[1] is that there has not been carried out a systematic investigation of the conditions under which a stable dilute solution of the alkali metal may be prepared. In the present investigation, the simpler sodium–Pyrex system is first studied. Evidence is presented which suggests that it is very difficult to remove adsorbed water from the Pyrex surface. It is the object of this research to study the effect of this adsorbed water on the stability of the blue solution at -78°C.

EXPERIMENTAL

Technique for transferring small quantities of sodium

In order to study the possible reactivity of a Pyrex surface under "strict" vacuum conditions (less than 10^{-6} cm of mercury as measured by a McLeod gauge) a simple technique was used for transferring small quantities of redistilled sodium to the surface of interest. This technique consisted of distilling sodium onto a glass ball which had a piece of iron imbedded in it. At room temperature the glass ball coated with sodium could be transferred by means of a magnet from region *A* to region *B* (Fig. 1) without coating the glass along the path of transfer. The mass of the glass enclosing the iron is important. It was of sufficient size so as to hold the sodium which had been distilled onto it. If the ball is too small, there is a danger that the sodium will be redistilled back onto the glass walls of the vacuum line.

Quantity of sodium transferred

It is useful to have some measure of the quantity of sodium distilled in this manner so that a relation can be made between various treatments of the pyrex surface and the quantity of gas evolved when the sodium is distilled on it. In different experiments the quantity of sodium transferred could be kept fairly constant by using similarly shaped glass balls and by taking care to coat the glass balls with sodium so that they had approximately the same colour characteristics. The amount of sodium distilled onto a glass ball was determined by reacting the sodium with excess degassed-water on the vacuum line. After completion of the reaction liquid nitrogen was used to freeze out the water vapour and the pressure of hydrogen was determined by a calibrated McLeod gauge. After the volume of the system was calibrated (1.30 l.) the moles of hydrogen evolved at room temperature were calculated by the ideal gas law. From this the moles of sodium distilled on the glass ball were calculated to be 10^{-6}.

---

* Present address: National Aeronautics and Space Administration, Lewis Research Centre, Cleveland, Ohio.

[1] KRAUS, *J. Chem. Educ.* **30**, 83 (1953).

Hydrogen evolution

It has been observed that a measurable quantity of hydrogen is evolved when sodium metal is distilled under vacuum conditions. Previous work[2, 3] indicates two possible sources for the hydrogen evolution. These two sources are degassing of the sodium during vacuum distillation and reaction of the sodium metal with adsorbed water on the Pyrex surface.

Treatment of Pyrex surface

In order to discover whether there is a correlation between preliminary treatment of the Pyrex surface and the pressure of the gas evolved when the sodium is distilled on it, the following procedure was used. In parts (3a) through (3d) four tubes as in Fig. 1 were arranged in series. The Pyrex surface was treated in the following ways:

(1) Not washing and baking out the glass on the vacuum line at 400°C for about 12 hr while pumping under "stick" vacuum conditions. (Fig. 1)

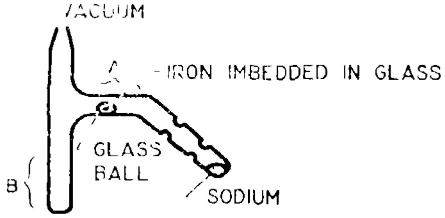


FIG. 1. Study of glass surface at region *B*.

(2) Cleaning with soap solution and rinsing with twice distilled water for an extended period of time (one to six days) and baking out the glass on the vacuum line at 400°C for about 12 hr while pumping under "stick" vacuum conditions. (Fig. 1)

(3a) Washing with twice distilled water for 1 hr and baking out the glass on the vacuum line at 400°C for about 12 hr while pumping under "stick" vacuum conditions.

(3b) Washing with reagent grade di-ethyl ether for 1 hr and baking out the glass on the vacuum line at 400°C for about 12 hr while pumping under "stick" vacuum conditions.

(3c) Washing with reagent grade ethanol for one hour and baking out the glass for about 12 hr at 400°C while pumping under "stick" vacuum conditions.

(3d) Washing with reagent grade tetrahydrofuron for 1 hr and baking out the glass for about 12 hr at 400°C while pumping under "stick" vacuum conditions.

Study of the effect of each treatment (1 *through* 3*d*). Onto each treated surface 10^{-6} mole of sodium was distilled. In each case an area of approximately 10 cm² of the treated surface was visually observed to be covered with the sodium film. This distillation was accomplished by using a yellow flame while pumping, sealing off the excess sodium twice at constrictions (Fig. 1), and finally distilling the sodium onto the glass ball in the vacuum system. The coated glass ball was transferred in the manner previously described to the part of the system to be studied. The quantity of gas liberated after distilling the 10^{-6} mole of sodium onto each treated surface was small, the pressure in each case was approximately 1×10^{-4} cm of Hg. To a first approximation, the quantity of gas liberated by distilling the sodium onto the treated glass surface was independent of the washing technique (1 through 3d). Samples of this gas were analysed using a mass spectrometer and found to consist of hydrogen.

As a final step in this procedure, part of the Pyrex system was baked out on the vacuum line for about 200 hr while pumping under "stick" vacuum conditions. After this treatment was completed, 10^{-6} mole of sodium was distilled, first on the surface that had been at 400°C, and second, on the glass surface that had been at room temperature. McLeod measurements indicated that a negligible amount of gas was given off in the first case, in the second case a measurable quantity of gas was evolved but less than the procedures involving 12 hr baking. This evidence suggests that hydrogen evolution is due to a reaction between sodium and strongly adsorbed water on the glass surface. This strongly adsorbed water may be almost completely removed from the surface heated at 400°C under the conditions described.

---

(2) J. STRONG, *Procedures in Experimental Physics* Chap. 13, p. 534 (Prentice-Hall, Englewood Cliffs, N.J. (1960))

(3) S. DUSHMAN, *Scientific Foundations of Vacuum Technique*, Chap. 8, p. 530. J. Wiley, New York (1949)

In order to have some independent means of checking this conclusion, the following procedure was used. A Pyrex ampule was treated with deuterium oxide for a period of six days to allow for exchange between the hydrogen and deuterium on the Pyrex surface. Then the ampule was placed on the vacuum line (Fig. 1) and baked for about 12 hr at 400 °C while pumping under "stick" vacuum conditions. About 10^{-6} moles of sodium was distilled onto the treated glass surface by the usual procedure. A small quantity of gas was evolved. A sample of this gas was found to consist of a mixture of H_2, HD, and D_2 in about equal proportions. The presence of HD and D_2 tends to rule out the possibility that all the gas evolved in the sodium distillation is due to a degassing of the sodium.

Preparation of blue solution

The preparation of a dilute solution of sodium in liquid ammonia at −78 °C was carried out by use of the previously described technique for transferring small quantities of sodium under "stick" vacuum conditions. The apparatus for the preparation of the solution consisted of an ampule with a side arm (Fig. 1). After the conditions of "stick" vacuum and a negligible leak rate had been established, sodium was distilled onto the glass ball contained in the side arm (region *A*, Fig. 1). 3 ml of the ammonia solvent, which had been dried over potassium, was distilled into the ampule (region *B*, Fig. 1). The solvent was degassed. The blue solution was prepared at −78 °C by transferring the coated glass ball from the side arm (region *A*) into the solvent (region *B*) by means of a magnet. After the blue solution was prepared, the glass ball was removed.

Evolution of gas

The blue solution was allowed to sit at −78 °C for 10 min, and then a liquid nitrogen bath was placed around the ampule containing the solution. The McLeod gauge indicated that a small amount of non-condensable gas was evolved, the pressure being about 10^{-4} cm Hg. A sample of this gas was identified as hydrogen by means of a mass spectrometer. Previous experiments had shown that the solubility of hydrogen in solid ammonia at liquid nitrogen temperature is negligible for pressures of hydrogen less than 10^{-2} cm (the range of interest).

The pressure was followed for an hour and observed to be constant. Varying up to an hour the lapse of time between the time when the blue solution was initially prepared at −78 °C and the time when the nitrogen bath was placed around the ampule containing the blue solution did not appreciably change the pressure of the gas evolved.

Variation of preparation

The method of preparation was varied to observe whether this affected the amount of gas evolved. Redistilled sodium was distilled directly onto the bottom of the ampule while pumping by use of the glass ball transference technique. Three cubic centimetres of degassed ammonia were distilled into the ampule, dissolving the sodium and forming a blue solution at −78 °C. Then a liquid nitrogen bath was placed around the ampule containing the solution. The amount of gas evolved was of the same order of magnitude as in the first preparation.

A third method of preparation was carried out by distilling 3 ml of degassed liquid ammonia into an ampule around which a liquid nitrogen bath was placed. A glass ball coated with redistilled sodium was transferred from the side arm of the ampule onto the solid ammonia. The liquid nitrogen bath was replaced by a dry-ice acetone bath and a blue solution was formed at −78 °C. The glass ball was removed from the blue solution. Then the dry-ice acetone bath was replaced by a liquid nitrogen bath. The McLeod gauge showed that a small amount of non-condensable gas was given off. Its pressure was of the same order of magnitude as in the two previous cases.

The following variations in procedure seem to make very little difference in the quantity of gas evolved:

(1) the length of time in which the ammonia solvent was dried at −78 °C over potassium (from one day to several weeks),
(2) baking out the glass from one day to several days at 400 °C while pumping under "stick" vacuum conditions,
(3) washing with liquid ammonia, (4) combining (2) and (3),
(5) the number of times sodium is redistilled (2 to 5 times).

However, washing the glass with a solution of sodium in liquid ammonia resulted in a decrease in the quantity of gas evolved as measured with a McLeod, but it did not eliminate entirely the hydrogen evolution.

The evidence presented in the study of the sodium-Pyrex system indicates that the hydrogen evolution is not due to a degassing of the sodium when it dissolves in liquid ammonia. The hydrogen evolution may be due to a chemical reaction. The two reactions which seem reasonable are

(1) a reaction between the blue solution and the adsorbed water at the glass liquid interface, (2) a reaction in which amide is formed

$$Na_{(sol)} + NH_{3(l)} \xrightarrow{-78°C} NaNH_{2(sol)} + \frac{1}{2} H_{2(g)}$$

The following experiment was carried out to study the combined effect that adsorbed water plus NaOH (a possible decomposition product in the first reaction) have in contact with a blue solution at −78°C. A glass ampule with two side arms was washed with D_2O for six days to allow for exchange on the surface. Sodium deuteroxide was prepared in this ampule on the vacuum line by the following procedure. Using the transference technique, sodium was reacted with excess degassed deuterium oxide on the vacuum line. After the reaction had been completed, the ampule was removed from the vacuum line and a new supply of sodium was introduced at the second side arm of the ampule. After the system was returned to the vacuum line the ampule containing the sodium deuteroxide was baked at 400°C for about 12 hr while pumping under "stick" vacuum conditions. The blue solution was then prepared in the presence of the base at −78°C. After sitting for about 10 min the blue solution was frozen by the liquid nitrogen bath. A small quantity of gas was evolved, a sample of which was analysed and found to consist of HD and H_2 in about equal proportions. After pumping off the gas, the system was allowed to warm up and the ammonia distilled into a second ampule which had been cleaned in the usual manner. The solvent was degassed and sodium was introduced into the ammonia forming a blue solution at −78°C. After sitting for about 10 min the blue solution was again frozen by placing a liquid nitrogen bath around the ampule. A small quantity of gas was evolved, a sample of which was analysed and again found to consist of HD and H_2 in about equal proportions. These results seem to indicate that the combined glass surface plus the sodium deuteroxide were not inert to the blue solution at −78°C. The reappearance of HD in two separate steps of the above procedure may indicate that the decomposition takes place via an exchange mechanism such as

$$\text{(a)} \qquad D_2O_{\substack{(glass,\\NaOH)}} + NH_{3(l)} \xrightleftharpoons{-78°C} OD_{\substack{(glass,\\NaOD)}} + NH_3D_{(sol)}$$

$$\text{(b)} \qquad 2Na_{(s)} + 2\,NH_3D_{(sol)} \xrightarrow{-78°C} Na_{\substack{(glass,\\NaOD)}} + NH_{3(l)} + NH_2D_{(sol)} + HD_{(g)}$$

Spectra of solution

In a recent study[1] of Beer's Law for sodium in liquid ammonia, it is stated that the blue solution is stable for long periods of time at −65°C or lower as indicated by spectral measurements. In addition, it is stated that it is more difficult to prepare a stable blue solution if it is too dilute. Thus the reaction which accounts for the "instability" of a dilute solution of sodium in liquid ammonia at −78°C must explain (1) the initial evolution of gas when the blue solution is prepared and (2) the stability of the blue solution as a function of concentration as reflected by spectral measurements.

The explanation which states that there is a reaction between the strongly adsorbed moisture and the blue solution satisfies the above two conditions. That is, the initial evolution of hydrogen is due to a reaction between the adsorbed moisture and the blue solution. After the moisture has been effectively removed from the glass liquid interface, the system is stable as indicated by the spectral measurements.

The explanation which states that the blue solution decomposes with the formation of sodium amide along with the evolution of hydrogen does not account in a simple manner for the apparent stability of the blue solution as reflected by the spectral measurements. The difficulty with this explanation is that it does not explain why the reaction stops after the initial decomposition in which hydrogen is given off.

Effect of sodium hydroxide on the spectra of the blue solution at −78°C

Since sodium hydroxide is a possible decomposition product of the reaction of sodium with adsorbed water, a small quantity of the hydroxide was introduced into a blue solution at −78°C and the effect on the stability of the solution observed.

The procedure for introducing a small amount of sodium hydroxide into the blue solution is as follows. Approximately $10^{-[illegible]}$ mole of sodium hydroxide were introduced into the open end of the U-shaped container shown in Fig. 2. The other end of the container had a small piece of iron imbedded in it. The U-shaped container could be introduced by means of a magnet into the cell region of the system. This system was placed on the vacuum line and pumped on for about 12 hr under "stick" vacuum conditions. The blue solution was prepared at −78°C by the usual technique of introducing $10^{-[illegible]}$ moles of sodium into 3 cm³ of the liquid ammonia. The spectra of the medium blue solution at −78°C was followed for about 45 min and found to be stable. Then the container with the sodium hydroxide was introduced into the solution. It was left in the solution during the spectral measurements but was not in the light path.

---

[1] J. L. DYE and R. C. DOUTHIT, *J. Amer. Chem. Soc.* **82**, 4472 (1960).

After an initial decomposition of about 6 per cent, assuming Beer's Law to a first approximation, the spectra were found to be stable over the time followed, which was about 45 min. This procedure was repeated for a light blue solution at −78°C. After an initial decomposition of about 66 per cent assuming Beer's Law to a first approximation, the spectra were again found to be stable over the time followed, which was about 45 min. In both cases, care was taken to avoid splashing when the hydroxide impurity was introduced into the blue solution at −78°C.

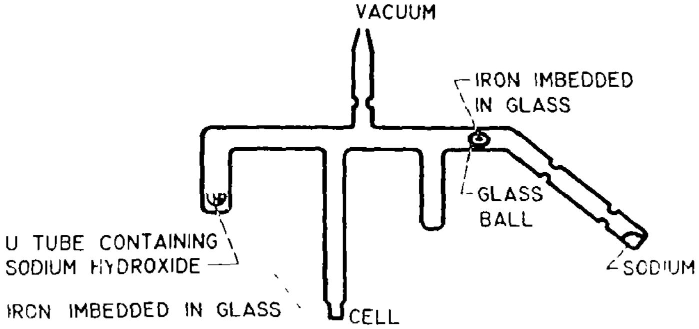


FIG. 2. Apparatus for introduction of sodium hydroxide into blue solution.

In the explanation which states that there is a reaction between the strongly adsorbed moisture and the blue solution, sodium hydroxide is a possible decomposition product along with the hydrogen evolved. The above results suggest that after an initial decomposition, probably due to adsorbed water on the *hydroxide*, the blue solution is stable in the presence of the hydroxide.

CONCLUSION

A simple transfer technique has been used to show that adsorbed water may be removed from a Pyrex surface when it is baked at 400°C for 200 hr while pumping under "stick" vacuum conditions. Additional experiments were done using heavy water. Analysis under conditions of baking at 400°C for 12 hr while pumping under "stick" vacuum conditions indicated the presence of D_2 and HD. The latter corroborates the presence of adsorbed water as the source of hydrogen evolution.

The evidence suggests that the instability of a dilute solution of sodium in liquid ammonia at −78°C is due to a reaction between adsorbed water and the blue solution. When the adsorbed water is effectively removed from the glass liquid interface, the blue solution is stable, as is reflected by spectral measurements.

Acknowledgements—The author gratefully acknowledges the contribution of Dr. O. SANIER in the mass spectrometer analysis.

J Inorg Nucl Chem 1963, Vol 25, pp 607 to 614 Pergamon Press Ltd Printed in Northern Ireland

THE RATIO OF THERMAL NEUTRON CAPTURE TO FISSION FOR ^{239}Pu

M J CABELL and L J SLEE
Chemistry Division, Atomic Energy Research Establishment,
Harwell, Didcot, Berks

(*Received* 23 *November* 1962)

Abstract—Alpha (the ratio of neutron capture to fission) for ^{239}Pu has been measured at seven different points along a flux scanning tube of the PLUTO reactor. Highly-enriched ^{240}Pu samples were also irradiated to make allowance for the destruction of this nuclide. Experimental values of α for ^{239}Pu varied from 0.458 to 0.470. Correcting all results to 2200 m/sec neutrons gave a mean value for α_0 of 0.370 ± 0.008 (standard error), a result which is in excellent agreement with present recommended values, but does not include uncertainties in the g and s values for neutron capture and fission.

DESPITE the dependence of the neutron economy of reactors on the values of alpha (the ratio of neutron capture to fission) for the primary fissile nuclides, measurements of this quantity for ^{239}Pu and slow neutrons have only been reported twice. Thus KANNE *et al.*,(1) as a result of measurements first described in 1955 but probably made as early as 1947, have concluded that alpha for the neutron spectrum of the Hanford reactor is 0.42 with a probable error of about 20 per cent. From this figure α_0, i.e. the value for 2200 m/sec neutrons, has been calculated to be 0.31 ± 0.09.(2) Again COCKING(3) has measured the ratio of the absorption cross section of ^{239}Pu to its fission cross section for almost mono-energetic neutrons of 0.0011 eV. This ratio, which can be equated to $(1 + \alpha)$ gave 0.300 ± 0.040 for alpha itself, a result which when corrected to 2200 m/sec neutrons gives $\alpha_0 = 0.30 \pm 0.10$.(2) We thus have two more-or-less directly measured values of α_0 for ^{239}Pu i.e. 0.31 ± 0.09 and 0.30 ± 0.10, which, although they are in agreement with each other, are both very imprecise. The present work was undertaken in an attempt to improve this situation.

Microgram quantities of a mixture of highly enriched ^{239}Pu and highly enriched Pu, diluted two-hundred-fold with an inert powder in order to minimize attenuation of the neutron density, were irradiated at several points along an aluminium tube which served as a high-flux irradiation position of the PLUTO reactor. Cobalt monitors were attached to each sample to measure the neutron dose it received. At the same time samples of a mixture of highly enriched ^{240}Pu and highly enriched Pu, also greatly diluted and also with monitors attached, were irradiated in similar positions adjacent to the ^{239}Pu-rich samples. When the irradiations were complete the neutron temperatures at two points along the irradiation tube were determined by the simultaneous irradiation of ^{59}Co, ^{238}U and ^{149}Sm monitors.

R KANNE, H B STEWART and F A WHITE *The Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva* 1955 Vol 4 p 315 United Nations (1956)

G SJÖSTRAND and J S STORY, *Nuclear Data for Reactor Design* Vol I Pergamon Press, to be published

J COCKING, *J Nucl Energy* **6**, 285 (1958)

The irradiated plutonium samples were freed from fission products by anion exchange chromatography and their isotopic compositions were compared with those of similar un-irradiated samples by means of a mass spectrometer In the case of the ^{239}Pu-rich samples it was thus possible to determine (a) the amount of ^{239}Pu which was destroyed by both neutron capture and fission combined (this is proportional to the absorption cross section of ^{239}Pu) and (b) the proportion of this quantity which was converted into ^{240}Pu which *was not subsequently destroyed* by neutron capture Similarly the results for the ^{240}Pu-rich samples showed the rate at which ^{240}Pu was destroyed so this information could be used to correct the results for the ^{239}Pu-rich samples in order that the *total* quantity of ^{240}Pu, irrespective of its final fate, formed in these samples throughout the irradiation could be determined also, this quantity is of course, proportional to the capture cross section of ^{239}Pu

The experiments thus gave a direct measurement of the ratio of the absorption cross section of ^{239}Pu to its capture cross section for a variety of reactor spectrum conditions and since this ratio is equal to $(1 + 1/\hat{\alpha})$ $\hat{\alpha}$ could be determined (the circumflex indicates an effective value for a reactor spectrum) Given $\hat{\alpha}$ and the spectrum parameters which were also measured, α_0 could be obtained also

CALCULATIONS

Let us suppose that a target material is chosen in which the initial number of atoms of ^{239}Pu ^{240}Pu ^{241}Pu and ^{242}Pu are $N_{9,0}$, $N_{0,0}$, $N_{1,0}$ and $N_{2,0}$ respectively, and that after irradiation with a dose of t neutrons per cm^2, the corresponding numbers are N_9 N_0 N_1 and N_2 If we define $N_{9,0}/N_{2,0}$ as R_1 N_9/N_2 as R_2, $N_{0,0}/N_{2,0}$ as R_3, N_0/N_2 as R_4 and $N_{1,0}/N_{2,0}$ as R_5, then it can be shown that

$$\hat{S}_9/\hat{\sigma}_9 = (R_1 - R_2A)/(R_4A - R_3\exp(-\hat{\sigma}_0 t))(1 - B) \tag{1}$$

in which

$$\begin{aligned} A = N_2/N_{2,0} = {} & \exp(-\hat{\sigma}_2 t) + R_5\hat{\sigma}_1[\exp(-\hat{\sigma}_2 t) - \exp(-\hat{S}_1 t)]/(\hat{S}_1 - \hat{\sigma}_2) \\ & + R_3\hat{\sigma}_0\hat{\sigma}_1\begin{bmatrix} \exp(-\hat{S}_1 t)/(\hat{S}_1 - \hat{\sigma}_2)(\hat{S}_1 - \hat{\sigma}_0) \\ -\exp(-\hat{\sigma}_0 t)/(\hat{S}_1 - \hat{\sigma}_0)(\hat{\sigma}_0 - \hat{\sigma}_2) \\ +\exp(-\hat{\sigma}_2 t)/(\hat{\sigma}_0 - \hat{\sigma}_2)(\hat{S}_1 - \hat{\sigma}_2) \end{bmatrix} \\ & + R_1\hat{\sigma}_9\hat{\sigma}_0\hat{\sigma}_1\begin{bmatrix} \exp(-\hat{S}_9 t)/(\hat{S}_1 - \hat{S}_9)(\hat{S}_9 - \hat{\sigma}_0)(\hat{S}_9 - \hat{\sigma}_2) \\ -\exp(-\hat{\sigma}_0 t)/(\hat{S}_1 - \hat{\sigma}_0)(\hat{S}_9 - \hat{\sigma}_0)(\hat{\sigma}_0 - \hat{\sigma}_2) \\ +\exp(-\hat{S}_1 t)/(\hat{S}_1 - \hat{\sigma}_2)(\hat{S}_1 - \hat{S}_9)(\hat{S}_1 - \hat{\sigma}_0) \\ +\exp(-\hat{\sigma}_2 t)/(\hat{S}_9 - \hat{\sigma}_2)(\hat{\sigma}_0 - \hat{\sigma}_2)(\hat{S}_1 - \hat{\sigma}_2) \end{bmatrix} \end{aligned} \tag{2}$$

B is proportional to the ratio of two series, as follows,

$$B = \hat{\sigma}_0 t\,\frac{[\frac{1}{2} - (\hat{S}_9 t + \hat{\sigma}_0 t)/6 + ((\hat{S}_9 t)^2 + (\hat{\sigma}_0 t)^2 + (\hat{S}_9 t)(\hat{\sigma}_0 t))/24 \quad]}{[1 - (\hat{S}_9 t + \hat{\sigma}_0 t)/2 + ((\hat{S}_9 t)^2 + (\hat{\sigma}_0 t)^2 + (\hat{S}_9 t)(\hat{\sigma}_0 t))/6 \quad]} \tag{3}$$

and the symbols S and σ indicate neutron absorption and capture respectively, the subscripts 9, 0, 1 and 2 indicate ^{239}Pu, ^{240}Pu, ^{241}Pu and ^{242}Pu respectively, and the circumflexes indicate reactions in a reactor spectrum

In order to calculate $\hat{S}_9/\hat{\sigma}_9$ then, it is necessary to know R_1, R_2, R_3, R_4 and $(\hat{\sigma}_0 t)$ as well as the factors A and B which correct for the loss of ^{242}Pu and ^{240}Pu by neutron capture during the irradiation and the simultaneous production of ^{242}Pu by successive neutron capture from plutonium isotopes of lower mass number. In addition it will be seen that B itself involves only $(\hat{S}_0 t)$ and $(\hat{\sigma}_0 t)$. Now, the atomic ratios can all be measured conveniently and precisely by means of a mass spectrometer. In addition $(\hat{S}_0 t)$ will also be known since it is determined by the other variables, thus

$$\exp(-\hat{S}_0 t) = R_2 A/R_1 \tag{4}$$

so that, apart from the factor A, it only remains to determine $(\hat{\sigma}_0 t)$.

Given the spectrum conditions of the irradiation positions, which could be measured independently, it would be possible to calculate $\hat{\sigma}_0$ (and hence $\hat{\sigma}_0 t$) since the variation of this quantity with neutron temperature and epi-thermal index is known fairly precisely.[1] We have preferred however to adopt the more reliable procedure of measuring $(\hat{\sigma}_0 t)$ independently in subsidiary experiments. For this purpose a mixture consisting almost entirely of ^{240}Pu and ^{242}Pu alone was prepared and aliquots were irradiated in positions adjacent to the other samples. For these mixtures the expression

$$R_1 A = R_3 \exp(-\hat{\sigma}_0 t) + R_1 \hat{\sigma}_0[\exp(-\hat{\sigma}_0 t) - \exp(-\hat{S}_0 t)]/(\hat{S}_0 - \hat{\sigma}_0) \tag{5}$$

was applied, and gave $(\hat{\sigma}_0 t)$ directly (the last term on the right hand side of equation (5) is very small and can be calculated). This information was then used further since, if we know $(\hat{\sigma}_0 t)$ and t (from the cobalt monitors) and hence $\hat{\sigma}_0$, it is possible to calculate the epi-thermal index of the irradiation positions from the dependence of $\hat{\sigma}_0$ on this quantity.[1]

All mass spectrometric measurements were made relative to ^{242}Pu whose concentration in the samples had been altered by up to 3.4 per cent by the irradiation. The correction term necessary to allow for this is the factor A involved in both equations (1) and (5) and defined by equation (2). In this last expression the first term on the right hand side, i.e. $\exp(-\hat{\sigma}_2 t)$, allows for the destruction of ^{242}Pu by neutron capture whilst the other terms allow for its simultaneous formation from plutonium isotopes of lower mass number. We have supplied the nuclear data necessary for the calculation of A from literature values where necessary and, although the dependence of $\hat{S}_0/\hat{\sigma}_0$ on the value assumed for A is not great, the lack of precision in A is nevertheless the largest single source of error in its determination. This fact will be discussed in more detail later.

Having obtained $\hat{S}_0/\hat{\sigma}_0$ by substitution in equation (1), this can be set equal to $(1 + 1/\hat{\alpha})$ and $\hat{\alpha}$ can be obtained. This is related to α_0 by the expression

$$\alpha_0 = \hat{\alpha}(g_f + r s_f)/(g_\gamma + r s_\gamma) \tag{6}$$

in which r is the epi-thermal index (obtained from a knowledge of $\hat{\sigma}_0$) and g and s are factors which describe departure from 1/v behaviour in the thermal and epi-thermal regions of the neutron spectrum respectively. The subscripts f and γ imply fission and neutron capture respectively. WESTCOTT[4] has listed values of g and s for ^{239}Pu as functions of the neutron temperature and epi-thermal index and we have used his tables for our calculations.

---

[4] C. H. WESTCOTT, Atomic Energy of Canada Ltd., Report CRRP 960 (3rd Ed. Corrected) (1960).

EXPERIMENTAL DETAILS

Many of the experimental techniques employed in this work have been discussed in detail in previous publications[1–4] so only where details differ will they be mentioned here.

1. *Mass spectrometric measurements*

All mass spectrometric measurements were made using an A.E.I. Type M.S.5 mass spectrometer. For each isotopic analysis about 0.1 μg plutonium was mounted on one of the side filaments of a tungsten triple-filament surface ionization source and under these conditions it was found that a satisfactory and sustained mass spectrum could be obtained with centre and side filament currents of about 6 A and 3 A respectively.

2. *Target materials*

Samples of three highly enriched plutonium isotopes, ^{239}Pu (99.9 per cent), ^{240}Pu (99.4 per cent) and ^{242}Pu (98.1 per cent), were supplied by the Electromagnetic Separation Group of the Chemistry Division, A.E.R.E., and these were blended to give mixtures of the appropriate isotopic composition. For the ^{239}Pu-rich target material R_1 was chosen such that it would approximate to $1/R_1$ thus avoiding making either ratio either very large or very small. For the ^{240}Pu-rich target material R_1 was chosen to be approximately unity since this condition minimizes random errors in the measurement of the difference between two approximately equal ratios.

In order to eliminate possible errors arising from source variations, five separate mass spectrometric sources were prepared from each target mixture and, for each, at least twenty consecutive measurements were made of each isotopic ratio of interest. The results for each source were then averaged and the averages weighted proportionally to the reciprocal of their variances to give final weighted means. In this way R_1, R_3 and R_2 were found to be 0.00740 ± 0.00004, 1.1660 ± 0.0002 and 0.00855 ± 0.00003 respectively for the ^{240}Pu-rich targets and 4.3539 ± 0.0048, 0.01332 ± 0.00018 and 0.00406 ± 0.00001 respectively for the ^{239}Pu-rich targets; for these latter it was also shown that the number of ^{238}Pu atoms was less than one for every ten thousand ^{239}Pu atoms.

3. *Irradiations*

For the irradiations the plutonium mixtures were diluted with 200 times their own weight of silica. About 500 μg plutonium in 2 ml nitric acid were slurried with 100 mg precipitated silica, the mixture was evaporated slowly to dryness with frequent stirring, and finally heated to 800. Approximately 10 mg of the plutonium-laden powder were taken for each irradiation and sealed in a silica tube. ^{59}Co, ^{238}U and ^{149}Sm monitors were also prepared as described previously.[5,6]

The aluminium flux scanning tube attached to the side of the fuel element B2 of the PLUTO reactor was used for irradiations. Eleven samples, each packed, together with a cobalt monitor, inside a small irradiation can, were strung together and lowered into the flux scanning tube for an irradiation of forty-seven days. Numbering the cans from the top downwards, cans 3, 6 and 9 contained ^{240}Pu-rich samples and the rest ^{239}Pu-rich samples.

Immediately after the irradiation of the samples had been completed, the neutron temperature at two points along the tube (positions 4 and 8) were measured by the simultaneous irradiation of ^{59}Co, ^{238}U and ^{149}Sm monitors.

4. *Post-irradiation treatment*

After irradiation the sample cans were transferred to a lead-shielded cell, opened by remote control, and the cobalt monitors were removed for separate measurement. Each sample tube was broken open by percussion, the contents were transferred to a platinum dish, treated with hydrofluoric and perchloric acids to remove the silica, and the plutonium was recovered in 2 ml of 8 M nitric acid. This solution was then fed to a glass column containing 100 mg De-acidite FF upon which the plutonium was absorbed whilst allowing the bulk of the fission products to pass through. The

---

(5) M. J. CABELL and L. J. SLEE, *J. Inorg. Nucl. Chem.* **24**, 1493 (1962).

(6) M. J. CABELL and L. J. SLEE, *J. Nucl. Energy*, Parts A/B, **16**, 195 (1962).

decontamination of the plutonium was completed by eluting the column with 8 M nitric acid and the plutonium was then recovered by passing 5 ml of a solution, 1 M in hydrochloric acid and 0.1 M in hydroxylamine hydrochloride, through the column. This eluate was evaporated to dryness and the plutonium was eventually recovered in a small volume of nitric acid. Finally a suitable aliquot was evaporated to dryness on a microscope slide and the residue was transferred as an aqueous suspension to the side filament of a mass spectrometric source.

Contamination of the irradiated samples by plutonium of a different isotopic composition was rendered unlikely by the fact that only new apparatus was used and the shielded cell had never contained plutonium before. The possibility was eliminated entirely by putting unirradiated samples of plutonium through the separation process when it was found that their isotopic composition was unaltered.

RESULTS

The neutron temperatures measured for positions 4 and 8 were 107° and 106° respectively. We have assumed a temperature of 106° for all samples.

The results for the ^{240}Pu-rich samples are given in Table 1 in which the factor A of column 3 is defined by Equation (2) and the factor C of column 4 is the term $R_1\hat{\sigma}_9[\exp(-\hat{\sigma}_0 t) - \exp(-\hat{S}_9 t)]/(\hat{S}_9 - \hat{\sigma}_0)$ of Equation (5). The neutron doses of column 6 were given by the cobalt monitors and allow the calculation of $\hat{\sigma}_0$. The epi-thermal indices of column 8 were obtained from the expression

$$\hat{\sigma}_0 = (286 \pm 7)(1.0536 + 38.66r) \text{ barns} \tag{7}$$

for which the thermal capture cross section quoted by Hughes *et al.*(7) and the g and s factors given by Westcott(4) have been used. Epi-thermal indices measured in this way gave results which were in satisfactory agreement with those obtained by making cadmium ratio measurements of gold with the reactor running at low power.

Table 1 – Results for the ^{240}Pu–^{242}Pu mixtures

Sample position	R_1	A	C	$\exp(-\hat{\sigma}_0 t)$	t (neutron/cm^2)	$\hat{\sigma}_0$ (barns)	r
3	0.9072	0.9884	0.00068	0.7685	2.807 × 10^{20}	938.3	0.0576
6	0.8263	0.9860	0.00076	0.6981	3.324 × 10^{20}	1081.3	0.0705
9	0.8286	0.9864	0.00076	0.7003	3.361 × 10^{20}	1059.8	0.0686

The results for the ^{239}Pu-rich samples are given in Table 2. In this table the isotopic ratios R_2 and R_4 were obtained, as with all isotopic ratios for irradiated samples, by preparing duplicate or triplicate sources, making at least twenty consecutive

Table 2 – Alpha for a reactor spectrum and for 2200 M/sec neutrons

Sample position	R_2	Epi-thermal index	$t \times 10^{-20}$ (neutron cm^{-2})	$\exp(-\hat{\sigma}_0 t)$	t	R_4	$\hat{\sigma}_0$ (barns)	$\exp(-\hat{S}_9 t)$	B	$\hat{S}_9/\hat{\sigma}_9$	$\hat{\alpha}$	α_0
1	3.251	0.0490	2.369	0.9800	0.9817	0.3465	843.0	0.7330	0.1089	3.1837	0.4579	0.3717
4	2.963	0.0619	3.026	0.9695	0.9730	0.4238	985.9	0.6622	0.1685	3.1277	0.4700	0.3760
5	2.838	0.0662	3.298	0.9650	0.9696	0.4478	1033.6	0.6320	0.1956	3.1557	0.4639	0.3693
	2.730	0.0699	3.449	0.9617	0.9671	0.4708	1074.1	0.6064	0.2153	3.1609	0.4628	0.3670
8	2.744	0.0693	3.506	0.9614	0.9669	0.4706	1066.9	0.6094	0.2173	3.1332	0.4658	0.3721
10	2.845	0.0680	3.227	0.9650	0.9694	0.4458	1052.6	0.6335	0.1948	3.1600	0.4630	0.3679
11	2.889	0.0673	3.191	0.9656	0.9699	0.4345	1045.5	0.6436	0.1906	3.1647	0.4620	0.3674

D. J. Hughes, B. A. Magurno and M. K. Brussel, BNL 325 (2nd Ed.) Supplement No. 1 (1960).

measurements of each isotopic ratio of interest for each source and averaging the two sets of results using the reciprocals of their variances as weighting factors Agreement between replicate analyses was usually to within one part in three hundred or better

The epi-thermal indices and ^{240}Pu effective cross sections of columns 3 and 8 of the table were obtained by interpolation from the results for the ^{240}Pu-rich samples and the calculations of α_0 from $\hat{\alpha}$ (columns 12 and 13) was made by means of equation (6) using the WESTCOTT g and s factors appropriate for 106 (4)

An examination of equation (2) shows that, apart from the factor exp ($\hat{\sigma}_2 t$), all the terms needed for the calculation of A (column 6) are dependent on the value assumed for $\hat{\sigma}_1$ We have used the expression

$$\hat{\sigma}_1 \quad (371 \pm 22)(1\ 0992 + 1\ 0088r) \text{ barns} \tag{8}$$

which is based on a thermal cross section due to STORY(8) and g and s factors derived by WESTCOTT(4), to calculate this We shall discuss the derivation of the factor exp ($\hat{\sigma}_2 t$) later

The seven results for α_0 listed in Table 2 give a mean value of 0 3702 with a standard error of ± 0 0013 which is due entirely to statistical variation It should be noticed that there is no obvious trend in the values for α_0 with increasing epi-thermal index such as would indicate a systematic error in the measurement of this quantity

ERRORS

An examination of equations (1), (2) and (3) for possible sources of systematic errors in the derivation of $\hat{S}_9/\hat{\sigma}_9$ will show that these can arise from the independent factors R_1, R_3, $(\hat{S}_0 t)$ and A It can further be shown that, with the data which have been quoted in this paper, the effects of the first three terms are small, they can only introduce errors of up to ±0 03 per cent, ±0 3 per cent and ±0 08 per cent respectively in $\hat{S}_9/\hat{\sigma}_9$ Moreover the effect of A can be divided into two parts, that due to the term exp ($-\hat{\sigma}_2 t$) and that due to the other terms of equation (2) which are dependent on the value assumed for $\hat{\sigma}_1$ Whilst the error in exp ($-\hat{\sigma}_2 t$) is appreciable the sum effect of the other terms is a possible error of only ± 0 06 per cent in $S_9/\hat{\sigma}_9$

In calculating exp ($-\hat{\sigma}_2 t$) the difficulty lies in knowing the value to adopt for $\hat{\sigma}_2$ Only two measurements of use here have been made of the variation in the capture cross section of ^{242}Pu with neutron energy Thus COTÉ *et al*,(9) using an 88 5 per cent sample of the nuclide, measured the variation in its total cross section from just above thermal energies to several keV and found that only two resonances, with peaks at 2 65 eV and 53 6 eV, dominate this region The carefully measured resonance parameters were used to calculate a resonance capture integral of 1050 ± 150 barns and a contribution of 19 2 ± 3 3 barns to the 2200 m/sec cross section, but, unfortunately, direct measurements in the thermal region were not possible

Again, BUTLER *et al* (10) have used a rather indirect activation method to measure the integral capture cross sections of ^{242}Pu in both the sub-cadmium and epi-cadmium regions of a reactor spectrum Correcting their results in the light of more precise values for the subsidiary nuclear data used in their calculations gives 19.8 ± 1.1 barns and 1380 barns for the 2200 m/sec capture cross section and resonance capture integral respectively.[8] Thus, whilst the thermal cross sections given by the two measurements are in agreement, the resonance integrals are not. To resolve this dilemma we have assumed the BUTLER *et al.* figure for the thermal cross section, since this was obtained by direct measurement, but have preferred the COTE *et al.* data for the resonance integral since the method used to obtain it was both more direct and less liable to error. Thus, in the terms of WESTCOTT's convention,[4] the effective cross section of ^{242}Pu is given by

---

(8) J S STORY *Private communication* (1962)

(9) R E COTÉ, L M BOLLINGER, R F BARNES and H DIAMOND, *Phys Rev* **114**, 505 (1959)

(10) J P BUTLER, M LOUNSBURY and J S MERRITT, *Canad J Phys* **35**, 147 (1957)

$$\hat{\sigma}_2 = (19.8 \pm 1.1) + (1041 \pm 150)r\sqrt{(4T/\pi T_0)} \text{ barns}$$

which, for a neutron temperature of 106° becomes

$$\hat{\sigma}_2 = (19.8 \pm 1.1) + (1335 \pm 192)r \text{ barns}$$

and it follows that the value taken for $\hat{\sigma}_2$ may be in error by as much as 12 per cent, this, together with the uncertainty in the neutron dose, is reflected as a possible error of ± 0.9 per cent in $\hat{S}_9/\hat{\sigma}_9$.

In total then, the uncertainty in $\hat{S}_9/\hat{\sigma}_9$ is 1.0 per cent and this is equivalent to an uncertainty of 1.4 per cent in $\hat{\gamma}$.

In order to calculate α_0 from $\hat{\gamma}$ it is necessary to know the neutron temperature and epi-thermal index. Although the two neutron temperature measurements gave results which agreed so closely (106° and 107°), we believe the agreement is fortuitous and an uncertainty of ± 15° is possible, this would give an error of ± 0.9 per cent in α_0. Similarly the systematic error in determining r is only ± 4 per cent but we have assumed a possible error of ± 10 per cent to allow for the uncertainties of interpolation and in the assumption that the measured epi-thermal index can be used as an average value appropriate to the whole irradiation. A 10 per cent error in r gives an uncertainty of ± 0.7 per cent in α_0.

Lastly we have assumed a possible error of ± 0.1 per cent in the measurement of isotopic ratios of heavy nuclides differing by one mass unit due to mass discrimination in the mass spectrometer.

To conclude, systematic errors in α_0 may arise as follows:—

from the determination of $\hat{\gamma}$	1.4 per cent
from uncertainty in the neutron temperature	0.9 per cent
from uncertainty in the epi-thermal index	0.7 per cent
from mass discrimination in the mass spectrometer	0.1 per cent

Combining in quadrature this gives a total uncertainty of ± 1.8 per cent. If this is now combined with the random error, and uncertainties in WESTCOTT's g and s values for ^{239}Pu are neglected, a final result for α_0 of 0.3702 ± 0.0080 is obtained.

DISCUSSION

It has been pointed out that the only previous direct measurement of α_0 for ^{239}Pu have yielded the values 0.31 ± 0.09[1] and 0.30 ± 0.10[2] respectively, our figure of 0.370 ± 0.008 is consistent with these. For a more precise comparison figure however we must look to indirect methods for obtaining alpha from its relationships with other directly measurable nuclear parameters. Of these, the most important is the fact that the ratio of the absorption to the fission cross section (both of which can be measured independently of either each other or alpha) gives $(1 + \alpha)$ directly. As a result of relationships such as these a "world consistent set" value for alpha for ^{239}Pu has been obtained and is 0.39 ± 0.03 at present.⁽⁷⁾ Similar considerations using more recent and reliable data have led SJOSTRAND and STORY to recommend a value of 0.386 ± 0.013. It will be seen that our result is an excellent agreement with both these figures.

The only errors we have not taken into account in our results are those which arise from using the g and s values given in WESTCOTT's tables⁽⁴⁾ for neutron capture and fission in ^{239}Pu. It is difficult to determine exactly what these errors are. However, the g and s factors are not fixed, but depend on the best differential cross section data available at the time of calculation; they will therefore alter with time and it is to be expected that they will differ from the true values by progressively smaller amounts. In this respect it is significant that with data taken from the three editions of WESTCOTT's tables so far published (covering a period of four years) the factors necessary to correct the $\hat{\alpha}$'s given in this paper to α_0 have altered by only 1½ to 1¼ per cent.

Rather than guess at the errors associated with g and s we have preferred to quote a final result which does not include them and to set out the individual results in such a way that should the factors be altered slightly in the future, amended values of α_0 may be calculated simply.

Acknowledgement—Grateful acknowledgement is made to Mr. D. AVERY for his help with some of the mass spectrometric measurements.

J. Inorg. Nucl. Chem. 1963. Vol. 25, pp. 615 to 617. Pergamon Press Ltd. Printed in Northern Ireland

THE PILE NEUTRON FISSION YIELDS OF ^{127}Sb AND ^{129}Sb

F. HAGEBØ
The Gustaf Werner Institute, University of Uppsala, Uppsala, Sweden

(*Received* 15 *October* 1962, *in revised form* 8 *December* 1962)

DURING a study of the β^-/IT-branching of 33 day ^{129m}Te, ANDERSSON and HAGEBØ(1) found that previously determined(2–4) fission yields in the mass 129 chain were inconsistent especially after the determination of the branching of 14·6 per cent from ^{129}Sb to ^{129m}Te by PAPPAS and WESTERLUND(5). GRUMMIT(6) and PAPPAS(2) have both measured the fission yield of ^{129}Sb and found 0·2 and 0·4 per cent respectively. These values were taken to be lower limits, as the half life of the tin parent was unknown. NOVEY(4) and PAPPAS(2) measured the fission yield of ^{129m}Te and obtained values of 0·19 and 0·35 per cent respectively, and finally PURKAYASTHA and MARTIN(3) have measured the fission yield of ^{129}I by neutron activation and obtained 0·9* per cent.

An attempt was therefore made to measure the cumulative yield of 4·34 hr ^{129}Sb,(7) as this nuclide is expected to represent about 98 per cent of the total chain yield from charge distribution considerations.(2)

The yield of 4·34 hr ^{129}Sb was determined relative to 93 hr ^{127}Sb mainly by counting their respective daughters, i.e. 67 min ^{129g}Te and 9·3 hr ^{127g}Te. The latter nuclides were isolated from their antimony precursors after a suitable growing in time. This approach was used instead of direct counting of antimony because of the greater simplicity of the resulting decay curves and because the tellurium decay schemes are better known. Direct counting of one antimony sample, however, gave the same result as the indirect approach. To check the previously measured fission yield of ^{127}Sb,(2,8) ^{140}Ba was in two experiments used as a monitor.

Quite recently, HAGEBØ, *et al.*(9) have shown that ^{127}Sb and ^{129}Sb each have two tin precursors 4·6 min and 2·2 hr ^{127}Sn and 8·8 min and 1·0 hr ^{129}Sn, and the same authors estimated the ratio between the yields of 8·8 min ^{129}Sn and 1·0 hr ^{129}Sn to be 9–10, and between the yields of 2·2 hr ^{127}Sn and 4·6 min ^{127}Sn to be 3–4. Using 9 and 3 for these two ratios, combined with the expected yields from the charge distribution given by PAPPAS(2) we obtain about 8 per cent of the total chain yield for 1·0 hr ^{129}Sn and about 30 per cent for 2·1 hr ^{127}Sn.

---

* The author is indebted to Dr. G. R. MARTIN for an instructive private communication concerning some of the data given in reference (3).

G. ANDERSSON and F. HAGEBØ *Arkiv Fysik*, **22**, 349 (1962).

A. C. PAPPAS, Report AECU-2806, MIT-LNS-63 (1953). (Inaugural Dissertation University of Oslo.)

B. C. PURKAYASTHA and G. R. MARTIN, *Canad. J. Chem.* **34**, 293 (1956).

B. NOVEY, *Radiochemical Studies: The Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN) NNES Plutonium Project Record Div. IV Vol. 9 p. 976 McGraw-Hill, New York (1951).

A. C. PAPPAS and E.-A. WESTERLUND Private communication (1961).

I. GRUMMIT Personal communication to PAPPAS.(2)

[illegible] G. H. NEUMANN, O. MELIN and I. ALVAGER *Arkiv Fysik* **21**, 35 (1962).

W. ENGELKEMEIR, J. A. SEILER, E. P. STEINBERG and L. WINSBERG *Radiochemical Studies: The Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN), NNES Plutonium Project Record Div. IV, Vol. 9, p. 1372 McGraw-Hill, New York (1951).

HAGEBØ, A. KJELBERG and A. C. PAPPAS *J. Inorg. Nucl. Chem.* **24**, 117 (1962).

Standard equations of radioactive decay and growth were used(2) and the time for separation of antimony from the fission mixture and especially from tin, was so chosen that an uncertainty of 100 per cent in the estimated fractional chain yields for the tin precursors lead only to about 2 per cent uncertainty in the yield of antimony. This is the case for both ^{127}Sb and ^{129}Sb.

EXPERIMENTAL

$UO_2(NO_3)_2 \cdot 6H_2O$ p.a. was irradiated for 2 hr in the Stockholm reactor. After about 7 hr the target was dissolved in 3 M HCl with Sn (II) and Sb (III) carriers added. Te metal was precipitated by adding excess Te IV-carrier, and centrifuged off. This ensures an oxidation of Sn to the tetravalent state. Sb, Sn and Te sulphides were then precipitated with H_2S gas from 0·5 M HCl and the Sb and Sn sulphides dissolved in 6–8 M HCl. The solution was then diluted and adjusted to 7 M NH_4SCN and 0·5 M in HCl. Sn(IV) was removed from Sb by extraction of the former into ethyl ether at a predetermined time after the end of irradiation. The further purification of Sb was accomplished by a sulphide precipitation and isopropylether extractions as described by HAGEBØ *et al.*(9)

After the purification of Sb which was completed about 10 minutes after the separation from Sn, Te metal was precipitated from a hot 3 N HCl-solution containing Sb, using hydrazine dihydrochloride and sulphur dioxide. Centrifugation of the precipitate marks the start of growing-in of Te from Sb. After 9–12 hr new Te(IV) carrier was added and precipitated in the same way. PAPPAS and WESTERLUND(5) have shown that complete exchange occurs between the Te activity made by decay of Sb and Te(IV) carrier. The precipitate was dissolved in HNO_3 and reprecipitated twice. Te metal was filtered on to pretreated pre-weighed filter paper disks and chemical yield was determined by weighing before mounting on tape in a punched card.(2) The reduction to metal of Sb was performed using $CrCl_2$ and chemical yield determined as for Te.

Barium was in two cases isolated from an aliquot of the target solution, using the method of GLENDENIN.(10)

The counting was performed using an end window flow proportional counter. An aluminium absorber was used to absorb the conversion electrons from the metastable states. Correction factors for absolute β-counting were applied in a standard way and they were taken from the works of PAPPAS(2) and RUDSTAM.(11) The decay schemes adopted were those given in nuclear Data Sheets,(12) except for the case of ^{127}Sb. For this nuclide the β-energies given by DAY and VOIGT(13) were used as the γ-spectrum claimed by BOSCH and MUNCZEK(14) could not be verified.(7, 15)

The decay scheme of ^{129}Sb was for the single antimony sample counted, taken to be the same as for ^{127}Sb. This determination is therefore more uncertain than the others. The branching from Sb to the ground state in Te is measured by PAPPAS and WESTERLUND(5) and amounted to 0·854 for ^{129}Sb and to 0·796 for ^{127}Sb. The fission yield of ^{140}Ba is taken to be 6·35 per cent.(16)

---

(10) L. E. GLENDENIN, *Radiochemical Studies: The Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN) NNES Plutonium Project Record Div. IV, Vol. 9, p. 1657. McGraw-Hill, New York (1951).

(11) G. RUDSTAM, *Inaugural Dissertation*, Uppsala (1956).

(12) *Nuclear Data Sheets*, National Academy of Sciences, National Research Council, Washington 25, D.C.

(13) M. C. DAY, JR. and A. F. VOIGT, *Phys. Rev.* **101**, 1784 (1956).

(14) H. BOSCH and H. MUNCZEK, *Phys. Rev.* **106**, 983 (1957).

(15) E. HAGEBØ, Unpublished work.

(16) S. KATCOFF, *Nucleonics* **18**, No. 11, p. 201 (1960).

RESULTS

Table 1 summarizes the results obtained.

TABLE 1

Run	Element counted	$\bar{y}(127)$(%)	Ratio $\frac{y(129)}{y(127)}$
1	Sb–Te	0.138	7.16
2	Te	0.150	8.77
3	Te		7.80
4	Te		7.45
		$\bar{y}(127) = 0.144 \pm 0.008$	$\bar{R} = 7.80 \pm 0.70$

The errors quoted are standard deviations. From these data the fission yield of ^{129}Sb is calculated to 1.12 per cent. The standard deviation of this value is estimated to be 15 per cent, the main contribution coming from uncertainties in the correction factors used in connection with the β-counting. The yield is much higher than the earlier reported values, i.e. 0.2(6) and 0.4 per cent,(2) because previous determinations were not able to take the tin parent into account. Calculation of the yield of ^{129m}Te assuming its formation in 14.6 per cent of the decays in ^{129}Te gives a figure of 0.164 per cent; this should be increased by (1 ± 1) per cent of the chain yield, to take into account the independent yield. The result is 0.17 per cent in good agreement with 0.19 per cent as measured by NOVEY.(4) The value 0.35 per cent given by PAPPAS(2) seems to be too high.

The measured yield of ^{127}Sb, 0.14 per cent fits well in between 0.13 and 0.15 per cent measured by ENGELKEMEIR *et al.*(8) and PAPPAS(2) respectively.

A fission yield of 1.12 per cent of ^{129}Sb seems to be on the high side if compared to the measured yield of ^{129}I, 0.9 per cent.(3) However, due to the rather large error limits given, the discrepancy is not serious.

Acknowledgements—The author wishes to thank professor THE SVEDBERG for interest in the work and for the excellent working facilities available, the staff of the Stockholm reactor for irradiations and professor A. C. PAPPAS for helpful comments during the preparation of the manuscript. The work has been supported by the Swedish Atomic Research Council.

J. Inorg. Nucl. Chem. 1963. Vol. 25. pp. 619 to 626. Pergamon Press Ltd. Printed in Northern Ireland

HOT ATOM CHEMISTRY OF HALOGENS ACTIVATED IN β-DECAY—II

BOND FORMATION BETWEEN RADIOIODINE AND TOLUENE

A. HALPERN
Department of Radiochemistry, Institute of Nuclear Research,
Polish Academy of Sciences, Warsaw 9, Dorodna 16

(*Received* 6 *April* 1962, *in revised form* 12 *November* 1962)

Abstract—The bond formation between toluene and ^{131}I or ^{132}I formed by the decay of ^{131}TeCl$_4$ or ^{132}TeCl$_4$ has been investigated. The total organic yield is higher in the case of ^{132}I, although its recoil is lower than that of ^{131}I. It is concluded that the reactivity of the radioiodine atoms activated by β,γ-decay depends on excitation and ionization, rather than on kinetic energy. The percentage yields of some organic products, as well as the effects of small concentrations of elemental iodine and allyl iodide was also studied. The hypothesis is advanced that atoms activated in β,γ-decay participate in "epithermal" reactions, and that formation of an excited intermediate complex occurs as an initial stage of the reaction.

FOR a better understanding of the high reactivity of the atoms resulting from nuclear transformations, an explanation of the relative roles of the recoil and of the electric charge is of the greatest importance. Studies on the chemical consequences of β- or β,γ-decay seem to be of particular interest from this point of view. In fact, the recoil of such atoms is frequently very small, although the positive electric charge, whatever its origin (shake off after β-emission, or internal conversion of γ-rays) should be considerable for atoms of medium or high mass.

In the previous paper[1] bond rupture in ^{131}Te-labelled dibenzyl telluride has been described. The result obtained indicate that in 98 per cent of the events the chemical bond is ruptured as a result of the $^{131}\text{Te} \rightarrow {}^{131}\text{I}$ transformation. The comparison of this result with the calculated ^{131}I-atom recoil spectrum[2] led to the conclusion that this exceptionally high probability of molecular disruption can not be explained by recoil alone. However, peculiar difficulties were encountered while studying the formation of new bonds by the ^{131}I atoms in this system, since dibenzyl telluride has an inclination to form addition compounds with iodine, consequently a considerable part of the ^{131}I activity was found in unidentified chemical forms. Besides, the action of scavengers might be abnormal, because of the precipitation of dibenzyl telluride during the fractionation procedure.

The present investigation was undertaken with the object of studying the bond formation between toluene and the ^{131}I or ^{132}I atoms formed by the decay of ^{131}TeCl$_4$ or ^{132}TeCl$_4$, respectively. A solution of tellurium tetrachloride in toluene does not have the disadvantages of dibenzyl telluride.

The β-particles emitted by ^{131}Te have the following maximum energies[3]: 2.15 MeV (42.3%), 1.68 MeV (16.2%) and 1.36 MeV (41.4%), while for ^{132}Te the maximum

---

A. HALPERN, R. SOCHACKA, *J. Inorg. Nucl. Chem.* **23**, 7 (1961).

A. HALPERN, *Nukleonika*. In press.

A. BEDESKU, O. M. KALINKINA, K. P. MITROFANOV, A. A. SOROKIN, N. W. FORAFONTOV and W. S. Shpinel, *J. Exp. Theor. Phys.* (*U.S.S.R.*), **40**, 91 (1961).

β-energies are[4] 0.28 MeV (60%) and 0.1 MeV (40%). The γ-energies are 0.16 MeV and 0.7 MeV for ^{131}Te, and 0.22 MeV and 0.13 MeV for ^{132}Te. It is clear that there is a considerable difference between the recoil spectra of the ^{131}I and ^{132}I atoms. This makes it possible to draw conclusions about the role of kinetic energy in the effects under discussion.

EXPERIMENTAL

Reagents

The toluene of analytical grade was shaken twice with concentrated sulphuric acid, then with distilled water until the acid reaction had disappeared, dried for a long time with $CaCl_2$ and then distilled through a column filled with P_2O_5. The carriers (methyl iodide, phenyl iodide and *p*-iodotoluene, all of analytical grade) were used without additional purification. The fractions separated from a mixture of hydrocarbons by azeotropic distillation, boiling between 71 and 74°C, and 98 and 103°C at 10 mm Hg will be called undecane and tridecane respectively.

Preparation of the radioactive tellurium tetrachloride

(i) $^{131}TeCl_4$. The chlorination of metallic tellurium (of spectral purity) was carried out in an all-glass apparatus. After all gaseous products, particularly the excess of chlorine, were removed from the apparatus using a slight vacuum, the tellurium tetrachloride was dissolved in toluene. The solution, clear and colourless, was transferred into quartz ampoules in a stream of dry nitrogen, and activated in a flux of 3 × 10^{11} neutrons cm^{-2} sec^{-1} in the thermal column of the reactor "EWA" over a period of 20 min. Under these conditions 25 min ^{131}Te is mainly formed, and only a small amount of other tellurium radioisotopes.

(ii) $^{132}TeCl_4$. Inactive sodium tellurite was added as a carrier to a solution of $Na_2{}^{132}TeO_3$, supplied by the Radiochemical Center, Amersham, and metallic tellurium was precipitated with SO_2 in 3 N hydrochloric acid, filtered off on a porcelain filter, washed thoroughly with hot water followed by ethyl alcohol, and dried in a stream of warm air. The radioactive tellurium obtained was chlorinated and the $^{132}TeCl_4$ was dissolved in purified toluene, as described above. The degassed samples were prepared by a series of cycles of freezing, evacuating and thawing.

Thus, the $^{131}TeCl_4$ and $^{132}TeCl_4$ have been prepared in different ways. Unfortunately, the first could not be prepared after the neutron irradiation of the metallic tellurium, because of the short half life of ^{131}Te and the rather long time required for synthesis. Solution of the tellurium tetrachloride after neutron irradiation was also impractical.

Fractionation of the radioactive products

Samples of radioactive tellurium tetrachloride dissolved in toluene were allowed to stand for 30–50 hr (time required for the establishment of the radioactive equilibrium $^{132}Te \rightarrow {}^{132}I$, and, obviously long enough to complete the decay of the 25-minutes ^{131}Te, as well as ^{38}Cl). The solution was then extracted with 0.1 M sodium sulphite to separate the inorganic activity, and with 3 N sulphuric acid to remove the tellurium. Then were added as carriers to the organic phase methyl iodide, phenyl iodide, p-iodotoluene, in 15 ml aliquots, with 5 ml of undecane and 15 ml of tridecane, and the organic mixture was distilled through the adiabatic column Jena-Glass No. 8140 at reduced pressure. Methyl iodide, phenyl iodide and iodotoluene were collected each as three successive 5 ml portions (CH_3I was distilled at room temperature and 60 mm Hg, C_6H_5I at 65–66°C and 10–11 mm Hg, $CH_3C_6H_4I$, together with undecane, at 80–82°C and 10–11 mm Hg). The middle portions of each fraction were used for the activity measurements. Finally, two additional portions of tridecane were collected (at 85–100°C and 9–10 mm Hg). However, a residue still remained in the flask which could not be distilled off under the above conditions. The activity of this residue was ascribed to unidentified high-boiling organic iododerivatives, which will subsequently be called "polymers".

Counting procedure

The ^{131}I activity was measured with a scintillation counter (NaI/Tl crystal). The ^{132}I activity was measured using a scintillation counter with a single channel pulse analyser. The discrimination used permitted the counting of all γ-rays of energy higher than 0.32 MeV. Therefore, the arrangement did not count any of the ^{132}Te radiation, even if some of this radioisotope was presented in the solution assayed.

---

[4] W. KUNZ and J. SCHINTLMEISTER, *Tabellen der Atomkerne*, Vol. 2 Berlin (1959).

RESULTS

Table 1 shows the percentage total organic yield of the ^{131}I as a function of the concentration of the elemental iodine added prior to neutron irradiation. Table 2—the same quantity as a function of the concentration of the allyl iodide added prior to neutron irradiation. Tables 3 and 4 contain similar data for ^{132}I. Here elemental iodide and allyl iodide had been dissolved in toluene before the tellurium tetrachloride. All the above functions are also presented in Fig. 1.

TABLE 1. ORGANIC YIELD OF ^{131}I AS A FUNCTION OF THE CONCENTRATION OF ELEMENTAL IODINE

System in which ^{131}I was formed			Total organic yield (%)
Solution		I_2, mole fraction	
0.07 M $^{131}TeCl_4$	in toluene	0	24.6 ± 2.7
	in toluene	5×10^{-4}	13.7 ± 0.5
	in toluene	2×10^{-3}	10.6 ± 1.3
	in toluene	7×10^{-3}	11.6 ± 2.3

TABLE 2.—ORGANIC YIELD OF ^{131}I AS A FUNCTION OF THE CONCENTRATION OF ALLYL IODIDE

System in which ^{131}I was formed			Total organic yield (%)
Solution		C_3H_5I mole fraction	
0.07 M $^{131}TeCl_4$	in toluene	0	24.6 ± 2.7
	in toluene	2.8×10^{-3}	55.7 ± 5.9
	in toluene	5.6×10^{-3}	59.3 ± 10.9
	in toluene	1.2×10^{-2}	88.3 ± 3.1
	in toluene	2.8×10^{-2}	90.1 ± 2.9

TABLE 3.—ORGANIC YIELD OF ^{132}I AS A FUNCTION OF THE CONCENTRATION OF ELEMENTAL IODINE

System in which ^{132}I was formed			Total organic yield (%)
Solution		I_2 mole fraction	
0.07 M $^{132}TeCl_4$ in toluene degassed samples		0	67.7 ± 1.9
0.07 M $^{132}TeCl_4$	in toluene	0	66.7 ± 1.7
	in toluene	5×10^{-5}	21.4 ± 1.1
	in toluene	5×10^{-4}	14.6 ± 0.5
	in toluene	1×10^{-3}	15.5 ± 1.6
	in toluene	2×10^{-3}	14.0 ± 1.2

TABLE 4.—ORGANIC YIELD OF ^{132}I AS A FUNCTION OF THE CONCENTRATION OF ALLYL IODIDE

System in which ^{132}I was formed			Total organic yield (%)
Solution		C_3H_5I mole fraction	
0.07 M $^{132}TeCl_4$	in toluene	0	66.7 ± 1.7
	in toluene	1×10^{-3}	65.9 ± 1.3
	in toluene	2.6×10^{-3}	63.3 ± 2.2
	in toluene	3.6×10^{-3}	66.0 ± 5.7
	in toluene	6.5×10^{-3}	73.4 ± 2.6
	in toluene	1.3×10^{-2}	78.4 ± 1.1
	in toluene	2.5×10^{-2}	86.0 ± 1.9
	in toluene	3.6×10^{-2}	91.6 ± 1.0
	in toluene	4.4×10^{-2}	94.0 ± 0.5

TABLE 5. DISTRIBUTION OF SOME ORGANIC PRODUCTS FROM $^{131}TeCl_4$ IN TOLUENE*

System in which ^{131}I was formed	Percentage			
	Methyl iodide	Phenyl iodide	Iodo-toluene	Polymers"
0.07 M $^{131}TeCl_4$ in toluene	11.5 ± 5.9	23.7 ± 5.9	28.8 ± 7.1	36.0 ± 7.1
0.07 M $^{131}TeCl_4$ in toluene + 5×10^{-4} mole fraction I_2	8.4 ± 4.8	22.9 ± 3.0	34.5 ± 8.6	34.3 ± 6.6
0.07 M $^{131}TeCl_4$ in toluene + 2×10^{-3} mole fraction I_2	10.1 ± 5.4	23.1 ± 10.0	33.2 ± 13.6	33.6 ± 13.0
0.07 M $^{131}TeCl_4$ in toluene + 2.8×10^{-3} mole fraction C_3H_5I	70.5 ± 2.1†	13.0 ± 8.9	10.5 ± 7.1	6.0 ± 0.4
0.07 M $^{131}TeCl_4$ in toluene + 5.6×10^{-3} mole fraction C_3H_5I	72.5 ± 1.0†	11.7 ± 3.1	10.7 ± 3.1	5.1 ± 0.1
0.07 M $^{131}TeCl_4$ in toluene + 2.8×10^{-2} mole fraction C_3H_5I	80.3 ± 0.8†	9.0 ± 2.6	5.0 ± 1.7	5.7 ± 1.7

* The total organic yield (24.6 per cent) has been taken as 100

† This fraction contains all the allyl iodide as well

TABLE 6.—DISTRIBUTION OF SOME ORGANIC PRODUCTS FROM ^{132}TeCl$_4$ IN TOLUENE[*]

System in which ^{132}I was formed	Percentage			
	Methyl iodide	Phenyl iodide	Iodo-toluene	"Polymers"
0.07 M ^{132}TeCl$_4$ in toluene	5.5 ± 0.7	47.1 ± 11.4	21.0 ± 7.1	26.4 ± 8.0
0.07 M ^{132}TeCl$_4$ in toluene + 1 × 10^{-3} mole fraction I_2	8.2 ± 5.3	47.1 ± 12.5	17.9 ± 2.5	26.8 ± 9.6
0.07 M ^{132}TeCl$_4$ in toluene + 3.6 × 10^{-2} mole fraction C_3H_5I	57.9 ± 9.1[†]	20.2 ± 7.0	11.4 ± 7.0	10.5 ± 5.4

[*] The total organic yield (66.7 per cent) has been taken as 100

[†] This fraction contains all the allyl iodide as well

In the two last tables the data are given for the percentage yields of several organic products, namely of methyl iodide, phenyl iodide, iodotoluene and "polymers". Table 5 contains the data for ^{131}I, and Table 6 for ^{132}I. To calculate the yields of these products the total organic yield, not the whole radio-iodine activity, was taken as 100 per cent.

DISCUSSION

Comparison of the recoil and the reactivity of radioiodine activated in β,γ-decay. The recoil energy of the ^{132}I atom is much lower than that of the ^{131}I atom, due to the difference of β-spectrum of ^{131}Te and ^{132}Te. However, the total organic yield of ^{132}I

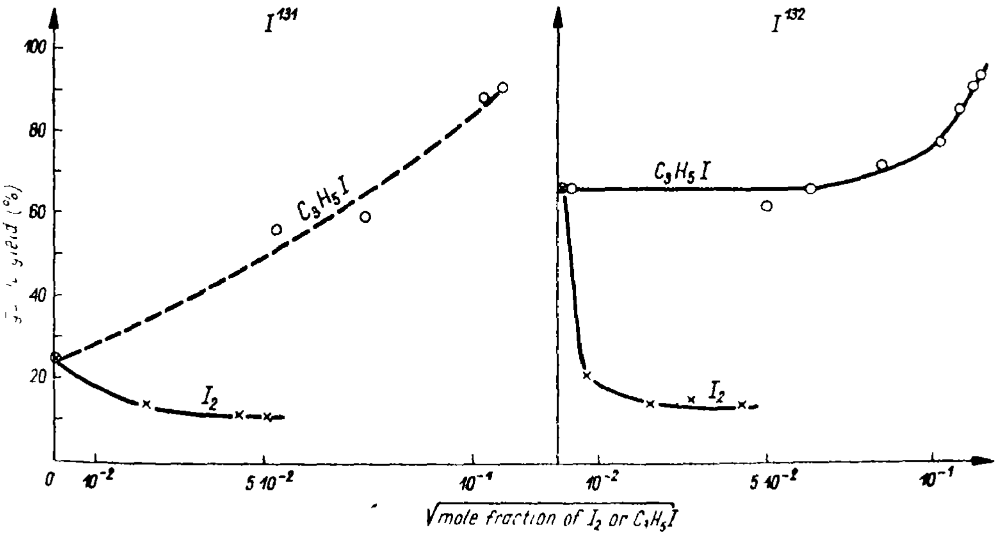


FIG. 1. Total organic yield of ^{131}I and ^{132}I as a function of the concentration of elemental iodine and allyl iodide.

is higher (66.7 per cent) than that of ^{131}I (24.6 per cent). From the above one may conclude that the reactivity of both radioiodine nuclides depends on the electrical charge and excitation of the orbital electrons, rather than on the kinetic energy.

It is very difficult to express the electronic excitation resulting from β-decay in energy units particularly when such complicated systems as atoms of medium atomic masses are involved(5). The possibility of evaluating the excitation of the product-atom on the basis of its chemical reactivity, even in a qualitative way, seems, therefore, to be of interest. In view of the results obtained here it may be concluded that the excitation of the ^{132}I is greater than that of the ^{131}I.

These and subsequent conclusions, however, are based on the comparison of results of two series of experiments, which differ in an important respect. ^{131}TeCl$_4$ was made by neutron irradiation of the toluene solution of tellurium tetrachloride, while ^{132}TeCl$_4$ was prepared separately and then dissolved in toluene. Under these circumstances it cannot be assumed that all the ^{131}Te produced is in the form of ^{131}TeCl$_4$ owing to the chemical effects of ^{130}Te(n, γ)^{131}Te reaction, as well as to the radiation reactions occurring in the reactor radiation field. Both these factors may cause some part of the ^{131}Te to react with the toluene. However, it has been found previously(1) that the covalent bond is always ruptured as a result of the ^{131}Te $\rightarrow$ ^{131}I transformation. Thus, even if some part of the ^{131}Te had been bonded organically before β-decay of the nuclide took place, all the ^{131}I is initially released from molecular combination. Besides, in several experiments the ^{132}TeCl$_4$/toluene solution was exposed to the action of the reactor radiation in the thermal column for a period of 20 min, and this procedure did not influence the value of the total organic yield of the ^{132}I.

Effect of the addition of elemental iodine on the total organic yield. The addition of approximately 10^{-1} mole fraction of elemental iodine to the toluene solution of radioactive tellurium tetrachloride decreases the total organic yield of ^{131}I from 25 per cent to 11 per cent, and that of ^{132}I from 67 per cent to 15 per cent, the reduced values being independent on the further increase in the iodine concentration. A possible explanation of this effect, following a suggestion of CAMPBELL(6), is that the process which is sensitive to added free halogen and which occurs with an insignificantly low activation energy is charge exchange between the recoiling ion and the molecule of added iodine

$$(I_{recoil})^{+} + II \rightarrow I_{recoil} + II^{+}$$

Consequently, the recoiling atom loses its unique properties resulted from the charge and stabilizes as a radioactive inorganic molecule. The decrease of the organic yield, which is larger in the case of ^{132}I than of ^{131}I, confirms the conclusion that the excitation and the percentage of charged atoms is greater in the first case.

Effect of addition of allyl iodide on the organic yield. The effect of small concentrations of allyl iodide on the organic yield supplies information about the initial kinetic energy of the recoil atoms. The effect depends on the rapid exchange of the radioactive thermal iodine atoms with allyl iodide(7). Therefore, the addition of allyl iodide leads to the production of labelled allyl iodide from all the thermal radio-iodine atoms, which normally end up in the inorganic as well as in the several organic forms. In our experiments the addition of (3–4) × 10^{-2} mole fraction of allyl iodide caused a considerable increase of the total organic yield namely to 90 per cent in the case of ^{131}I (Table 2 and Fig. 1), and to 94 per cent in the case of ^{132}I (Table 4 and Fig. 1). The data on the distribution of the several organic products, quoted in Tables 5 and 6, indicate indeed that only the fraction which contains the allyl iodide increases, while yields of other organic products decrease significantly. We could not investigate the effect of higher concentrations of allyl iodide since decomposition occurs, but we suppose that an increase of the total organic yield up to 100 per cent can be obtained. It seems clear from the above results that the significant majority of radioiodine atoms formed in β,γ-decay of radiotellurium, if not all of them, have a kinetic energy which lies in the thermal range, or only a little higher. The high chemical reactivity of such atoms depends on excitation and ionization, and they are able to participate in "epithermal" reactions, which depend on inelastic interactions with the molecules of the medium during which the energy of the atom is transferred to the vibrational and rotational energy states of the molecule, or, alternatively, in ionic or ion-molecule reactions.

---

(5) D. L. BAULCH and J. F. DUNCAN, *Quart. Rev.* **12**, 152 (1958).
(6) I. G. CAMPBELL, *Nukleonika* **3**, 43 (1958).
(7) W. H. HAMILL, R. R. WILLIAMS and H. A. SCHWARTZ, *J. Amer. Chem. Soc.* **72**, 2813 (1950).

Distribution of some organic products and consideration of the model. In connection with the results contained in Tables 5 and 6 the following points should be noticed.

Firstly, the organic iododerivatives identified might be considered as representative of several types of chemical processes. Thus, methyl iodide and phenyl iodide represent the products formed by a bond rupture between the benzene ring and the methyl radical and addition of radioiodine to the methyl radical in the first case and to the phenyl radical in the second, iodotoluene represents the product formed by the substitution in the ring without a bond rupture between the ring and the chain, finally, we did not investigate the nature of the "polymer" fraction, however its high boiling disposes us to treat it as a polymerized product formed after rupture of the benzene ring. The fact that the iodine activity was found in all the above chemical forms is a noteworthy example of the high reactivity of atoms activated in β,γ-decay. CUMMISKEY *et al.*[6] have recently expressed the opinion that ^{132}I from ^{132}Te decay exhibits a higher reactivity than radioiodine from thermal neutron capture.

Secondly, the yields (relative, i.e. calculated when the total organic yield is taken as 100 per cent) do not differ drastically in either case, which indicates that the distribution of products is but little dependent on the kinetic energy of the atoms.

Thirdly, the presence of elemental iodine in the system does not influence the relative distribution of organic products. This fact, probably suggests that all the organic products are formed in chemically similar processes. Indeed if some of them would be formed in homolytic reactions, while others in heterolytic ones, the yields of the first should decrease in the presence of iodine (because of the scavenging of radicals), the yields of the other being constant.

Fourthly, the addition of small amounts of allyl iodide reduces considerably the yields of all organic products. This bears witness to the fact that radioiodine atoms which are entering organic combinations have mostly thermal energies.

---

[6] CUMMISKEY, W. H. HAMILL and R. R. WILLIAMS *J. Inorg. Nucl. Chem.* **21**, 205 (1961).

Finally we wish to make some remarks on a possible model for the reactions of radioiodine atoms activated in β,γ-decay Such a model should take into account that the average kinetic energy of the atoms lies in the thermal or epithemal range, and that such atoms are positively, and probably multiply, charged This can be respected in the model which assumes that the radioiodine atom and the toluene molecule initially formed an excited intermediate complex (I $CH_3C_6H_5$) The formation of the complex is very probable because of the ion-dipole interaction between the radioiodine ion and the toluene (dipole moment 0 37 D) On the other hand at least two reasons may be mentioned for the instability of the intermediate complex Firstly, the kinetic energy supplied by the recoiling atom (of the order of 1 eV) transforms into the oscillation-rotary energy of the whole system Secondly, the energy of neutralization of the positively charged radioiodine ions causes the rupture of C H bonds inside the complex This process might be of particular importance in the case of multiply charged ions, when, consequently, the transferring of electrons occurs already inside the complex The electron transfer from the molecule to the ion is possible because of differences in the ionization potentials (8 5 V for toluene 10 6 V for the iodine atom, and 19 4 V for I^{+} ion)

Acknowledgement The author acknowledges with pleasure the stimulating discussions with Dr S SIEKIERSKI and the assistance with the experimental work of Mrs B KOSIAK Our thanks are due to the personnel operating the reactor I WA" at the Institute of Nuclear Research in Swierk near Warsaw for their cooperation in neutron irradiation

J. Inorg. Nucl. Chem. 1963. Vol. 25. pp. 627 to 630. Pergamon Press Ltd. Printed in Northern Ireland

FAST NEUTRON CAPTURE IN ^{232}Th

D. C. STUPEGIA, B. SMITH
Argonne National Laboratory, Argonne, Illinois
and
K. HAMM
Carthage College, Carthage, Illinois

(*Received* 17 *October* 1962)

Abstract—The capture cross section of ^{232}Th has been determined for monoenergetic neutrons in the energy range 0.19–1.1 MeV. The shape of the curve agrees closely with the theoretical curve predicted by LANE and LYNN,⁽¹⁾ showing a definite rise in cross section with increasing energy near 0.8 MeV.

LIKE many other even-even nuclides, ^{232}Th does not show a continuous decrease in radiative capture cross section with increasing neutron energy around 1 MeV. Nuclear theories, averaging the behaviour over many levels of the compound nucleus, predict that the cross section will vary as $1/E^{1/2}$ at lower energies and with a more complex dependence upon neutron energy, E, at higher energies. The cross section of ^{232}Th, however, has been found to rise with increasing neutron energy near 0.8 MeV, before resuming its expected decrease. This behaviour has been treated theoretically by LANE and LYNN⁽¹⁾ who fitted the ^{232}Th and ^{238}U data of HANNA and ROSE.⁽²⁾ That data, and the data of other workers, generally show a plateau in the cross section curve in the region in question, but the present results yield a curve whose shape is in closer agreement with the curve of LANE and LYNN.⁽¹⁾

METHOD

The neutron capture cross section of ^{232}Th has been determined as a function of neutron energy in the range 0.19–1.1 MeV by measuring the disintegration rate of 22.3 min ^{233}Th produced in a known mass of thorium exposed to a monoenergetic neutron beam of known intensity. The neutron beam was produced by bombarding lithium targets with protons from the 3 MeV Van de Graaff accelerator. The intensity was measured with a fission chamber, which counted fissions in a thin deposit of uranium enriched in ^{235}U. The irradiated thorium targets were counted in an end-window proportional counter, which detected the β-rays of ^{233}Th. The β-counting rates of the activated targets were related to the corresponding disintegration rates by counting, in the same geometry, thorium targets identical in form as those irradiated, into which had been introduced a sample of ^{233}Th, whose disintegration rate had been determined by liquid scintillation counting. Above the neutron energy 1.1 MeV the increasing fission of thorium produced enough fission product activity to interfere with the beta counting of ^{233}Th. Therefore, since fission products were not separated from the targets, 1.1 MeV was the upper limit of neutron energy in this work.

A. M. LANE and J. E. LYNN *Proc. Phys. Soc.* A **70**, 557 (1957).

R. C. HANNA and B. ROSE, *J. Nucl. Energy* **8**, 197 (1958).

EXPERIMENTAL

Preparation of targets

Thorium was separated from its daughters by extracting it from aqueous solution into a solution of thenoyl trifluoro acetone in chloroform. The thorium was then precipitated as the oxalate and ignited to oxide which was pressed into 1 cm diameter disks of mass about 0.3 g. Each batch of thorium so treated was sufficient for the preparation of about five targets which were irradiated before a new batch was prepared. This procedure minimized the time available for thorium daughters to accumulate, thereby reducing the interference by the latter with the beta counting of ^{233}Th.

Irradiations and flux monitoring

The neutron producing targets were deposits of metallic lithium on the inside of a tantalum cup of thickness 0.025 cm; their proton stopping power was 50 keV. The size of the proton spot on the lithium deposit was 0.3 cm by 0.6 cm, and the distance between the lithium target and the center of the thorium target was 1.7 cm. Proton currents were 20–30 μA and the irradiation times ranged between 16 and 40 min.

The fission chamber used to measure the neutron flux was a gas-flow parallel-plate ionization chamber, of thin-walled brass construction designed to minimize the effects of neutron scattering. The fissionable material was a 1 cm diameter deposit on 0.013 cm thick platinum of about 250 micrograms of enriched uranium (atom per cent: ^{235}U 93.27, ^{234}U 1.03, ^{236}U 0.483, ^{238}U 5.21). The thorium target and monitor lay flat against each other with their centers at 0 degrees with respect to the proton beam so that they subtended the same polar angle with respect to the neutron source. The uranium deposit faced into the counting volume of the fission chamber. The uranium monitor deposits were thin enough that there was no significant self-absorption of fission fragments in the monitor. Neutron absorption in the platinum backing and the thorium targets was entirely negligible. Total fissions were determined by recording the energy spectrum of the fission fragments with a 512-channel pulse-height analyser and summing the counts in this spectrum.

Calculation of the fission cross sections of the monitor sample included the effect of the minor percentages of uranium isotopes present, and the effect of the lower energy group of neutrons given by the ^{7}Li$(p, n)^7$Be reaction. The thorium cross sections were also corrected for the lower energy neutron group. The lower group neutron intensities were taken from BEVINGTON[3] *et al.*

Because the irradiation times were comparable to the half life of the activation product, fluctuations of proton current during the irradiation and the degradation of the lithium target, would adversely effect the results. To guard against this, the fission spectra were recorded in four separate 128-channel groups of the 512-channel analyser, each group corresponding to successive quarters of the total irradiation time. Fortunately the proton currents were steady and the lithium targets did not degrade appreciably: no complicated additional corrections were needed.

β-Counting of targets

After irradiation the thorium target was prepared for beta counting of ^{233}Th by mounting it on an aluminium plate, covering with a thin sheet of plastic, and placing it in a reproducible position in the counting chamber of an end-window proportional counter at about 25 per cent geometry. The maximum beta ray energy of ^{233}Th is 1.2 MeV. After separation of the thorium daughters, ^{228}Th remains with the target material and from it the major daughter activity grows. Nevertheless the newly prepared thorium targets had counting rates of only about 50 counts/min, increasing to about 160 counts/min by the time the batch of targets was irradiated and the ^{233}Th decay followed for 4 or 5 half-lives. The irradiated targets had counting rates between 10000 and 50000 counts/min at irradiation end, and 5 min counts were generally taken. To make an accurate subtraction of the daughter counting rate, one target of each batch was kept unirradiated and this one was counted in another proportional counter simultaneously with each count of the irradiated targets.

The counting rate of the ^{233}Th in the irradiated targets was related to the absolute disintegration rate in the following manner. Into a solution containing a known mass of thorium nitrate, from which the daughters had just been removed, was introduced a solution containing a known activity of ^{233}Th. Thorium oxalate was precipitated and ignited to oxide, which was made into disks of the same

---

(3) P. R. BEVINGTON, W. W. ROLLAND and H. W. LEWIS, *Phys. Rev.* **121**, 871 (1961).

shape and mass as the targets. With the mass of thorium in the disk and in the solution being known, the counting rate of the disk in the proportional counter yielded the desired factor. Since the thicknesses of the targets were about equal to the range of the 1.2 MeV β-rays of ^{233}Th, this calibration was done for several target thicknesses, in order to take into account the variation of the factor with the unavoidable small differences in target thickness.

Disintegration rate of ^{233}Th

The disintegration rate of the ^{233}Th solution used in the calibration of the proportional counter was measured by liquid scintillation β-counting. About 2 mg of thorium nitrate, whose daughters had been separated, was irradiated for 2 min in the thermal neutron flux of CP-5. The irradiated thorium was put into a solution of 0.1 N HCl, from which samples of various sizes were introduced into vials containing 15 ml of the scintillation solution. The latter consisted of a mixture, by volume, of 75 per cent dioxane, 12.5 per cent 1,2-dimethoxyethane and 12.5 per cent anisole, containing the scintillators 7 g/l of 2,5-diphenyloxazole (PPO) and 50 mg/l of (2-(5 phenyloxazolyl)) benzene (POPOP). In this counting system the light pulses in the scintillation solution are viewed by a phototube, and the resulting voltage pulses are amplified and analyzed by a 256 channel analyser.

RESULTS AND DISCUSSION

The capture cross sections are listed in Table 1 and plotted in Fig. 1. The errors are standard deviations, and the neutron energies for the present work refer to the center of the total range of neutron energies received by the thorium target. This energy spread is due to the 50 keV lithium targets and the variation of neutron energy with angle of emission with respect to the proton beam. The errors in the cross sections are composed of ±5 per cent in the fission cross section of the monitor, up to 0.5 per cent on the statistics of the fission counting, ±3 per cent in the accuracy of

TABLE 1.—NEUTRON CAPTURE CROSS SECTION OF ^{232}Th

Neutron energy (keV)	Spread (keV)	Capture cross section (millibarns)
191	38	217 ± 15
290	36	183 ± 13
394	36	164 ± 11
482	35	167 ± 11
491	37	193 ± 13
493	36	178 ± 12
493	36	182 ± 12
523	50	180 ± 17
590	36	188 ± 13
684	38	220 ± 15
689	39	197 ± 14
705	50	210 ± 20
785	32	213 ± 14
791	37	196 ± 13
809	50	180 ± 17
885	38	176 ± 12
887	43	195 ± 13
978	38	165 ± 12
988	38	152 ± 11
1086	39	152 ± 11
1091	39	156 ± 10
1170	43	152 ± 11

the absolute beta counting, ± 1 per cent in other errors in the calibration, up to 0 6 per cent in the counting statistics of irradiated targets, and about ± 2 per cent due to the uncertainty in the ^{233}Th half-life

The figure includes the experimental results of this measurement and of past work giving the data of Hanna and Rose,(2) Staviskii and Tolstikov(4), Barry *et al* (5) and Hughes and Schwartz (6) The theoretical prediction of Lane and Lynn(1) is also shown The agreement between the various sets of data is satisfactory below an incident neutron energy of 600 keV Above 600 keV the results of this work are in qualitative agreement with other measurements, excepting the results of Hanna and Rose (2) In detail, the work reported here indicates an increase in the capture cross section of ^{232}Th in the vicinity of 800 keV This rise is in good agreement with the prediction of Lane and Lynn(1) which considers only the competition of inelastic neutron scattering to the first two rotational levels of the ^{232}Th nucleus (2 +, 4 +) The qualitative effect of inelastic scattering to the next available residual nuclear states at about 800 keV and 1100 keV (Smith(7)) will be a marked decrease in the capture cross section above the respective inelastic thresholds due to the increased number of exit channels from the compound nucleus Such a decrease in the capture cross section of ^{232}Th above these inelastic thresholds is noted in the results of this experiment

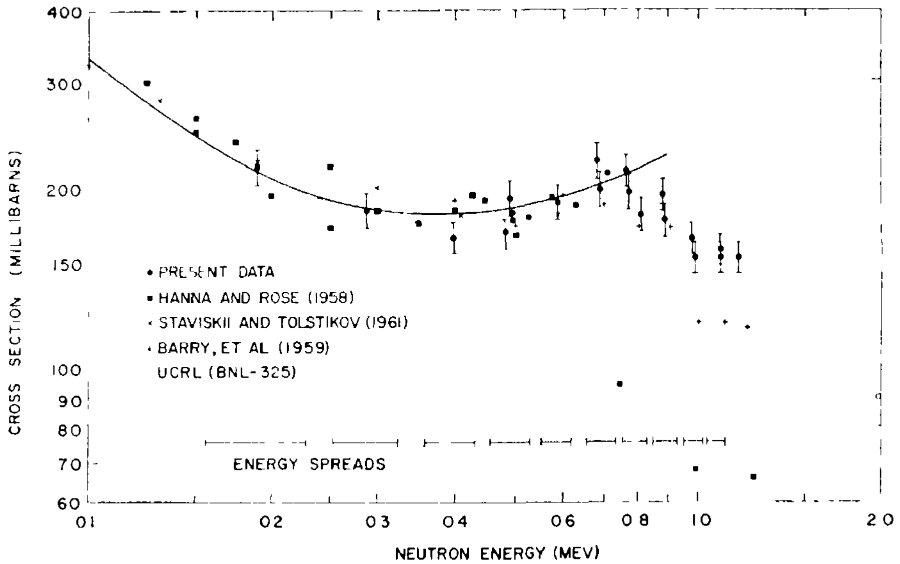


Fig 1 Neutron capture cross section of ^{232}Th The solid line is the theoretical curve of Lane and Lynn (1)

Acknowledgements One of us (K H) is grateful to Dr C E Crouthamel for arranging his recent visit to Argonne The authors are also grateful to Mr A A Madson and Miss M Jones for assistance in counting and data analysis

(4) Yu Ya Staviskii and V A Tolstikov, *Atomnaia Energiia* **10**, 508 (1961)

(5) J F Barry, L P O'Connor and J L Perkin, *Proc Phys Soc* **74**, 685 (1959)

(6) D J Hughes and R B Schwartz, *Neutron Cross Sections* BNL-325, 2nd Edn (1958)

(7) A B Smith, *Phys Rev* **126**, 718 (1962)

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 631 to 635. Pergamon Press Ltd. Printed in Northern Ireland

PHENYL LEAD (IV) AZIDES—PREPARATION, PROPERTIES AND INFRA-RED SPECTRA*

E. LIEBER†, C. N. R. RAO‡ AND F. M. KEANE
Department of Chemistry, Roosevelt University
Chicago 5, Illinois

(*Received* 30 *October* 1962)

Abstract—Two stable tetravalent lead azides, triphenyl lead azide and diphenyl lead diazide have been prepared and characterized. Physical properties such as crystal morphology, infra-red spectra, X-ray diffraction, solubility and thermal behaviour are reported.

FORMATION of tetravalent lead compounds and lead by the disproportionation of divalent lead compounds has been reported in the literature.(1, 2) It was felt that the photochemical yellowing of lead (II) azide, $Pb(N_3)_2$, may also possibly arise from its disproportionation to lead (IV) azide, $Pb(N_3)_4$ and metallic lead. Tetravalent lead compounds such as lead (IV) chloride(3) and lead (IV) acetate(4) have been isolated and characterized. However attempts(5, 6) to isolate pure lead (IV) azide have been hitherto unsuccessful and there are only qualitative indications of its formation. In this communication we report the preparation and characterization of two stable lead (IV) azides, I and II, where the phenyl groups on lead confer considerable stability to

$$\underset{\text{I}}{(C_6H_5)_3PbN_3} \qquad\qquad \underset{\text{II}}{(C_6H_5)_2Pb(N_3)_2}$$

these compounds. To our knowledge, these are the only stable lead azides known presently.

EXPERIMENTAL

Triphenyl lead chloride.(7) Tetraphenyl lead§ dissolved in hot chloroform (15 ml of chloroform per gramme of tetraphenyl lead) was placed in a three-necked flask fitted with a gas delivery tube so as to introduce the gas below the level of the chloroform solution while stirring. The flask was used as an open system. Dry hydrogen chloride was introduced while warming the mixture by means of a water-bath at 50–60°C. The hydrogen chloride was introduced until the appearance of a white precipitate (diphenyl lead dichloride). The mixture was then refluxed to complete the reaction between the hydrogen chloride and the tetraphenyl lead. The hot mixture was suction filtered through a water-heated funnel (55°C), Whatman No. 50 paper. Typical preparations yielded 1–3 per cent of diphenyl lead dichloride as a by-product. The solvent was removed from the filtrate by simple distillation from a water-bath. The residue was extracted with portions of hot absolute ethyl alcohol. The alcoholic filtrate was cooled to 0°C and the precipitate recovered by suction filtration (chilled apparatus). The yield of triphenyl lead chloride averaged 75–80 per cent over several runs. The combined yields were recrystallized from absolute ethanol at 0°C for the purpose of analysis. (Found:* C, 45.87; H, 3.20; Cl, 7.50. Calc. for $C_{18}H_{15}ClPb$: C, 45.61; H, 3.61; Cl, 7.48%.) The melting point† was 207°.

---

* This work was supported by Contract DA-44-009-ENG-4798, Basic Research Group, LRDL, Fort Belvoir, Virginia.

† To whom all correspondence should be addressed.

‡ Department of Physical Chemistry, Indian Institute of Science, Bangalore, India.

§ Prepared by the method of GILMAN *et al.*(8) Commercially available from Aldrich Chemical Co., Milwaukee, Wisconsin.

(1) E. KRAUSE and A. VON GROSSE, *Die Chemie der Metall-Organischen Verbindungen* (1937).

(2) R. W. LEEPER, L. SUMMERS and H. GILMAN, *Chem. Revs.* **54**, 101 (1954).

(3) U. F. POSTINIKOV and A. I. SPERANSKII, *J. Chem., U.S.S.R.* **10**, 1328 (1940).

(4) H. S. BOOTH, *Inorganic Synthesis*, p. 47. McGraw Hill, New York (1937).

(5) H. MOLLER, *Z. Anorg. Chem.* **260**, 249 (1949).

(6) E. LIEBER, Unpublished results.

(7) H. GILMAN and J. ROBINSON, *J. Amer. Chem. Soc.* **51**, 3112 (1929).

(8) H. GILMAN, L. SUMMERS and R. W. LEEPER, *J. Org. Chem.* **17**, 630 (1952).

Triphenyl lead hydroxide.(9) In 200 ml of absolute ethanol, 4.74 g (0.010 mole) of triphenyl lead chloride was dissolved in a water-bath. A sufficient volume (equivalent to 0.010 mole) of the alcoholic KOH was added to the warm alcoholic solution of the triphenyl lead chloride. The reaction mixture was stirred rapidly for one hour by means of a magnetic stirrer and poured into 400 ml of warm, carbon dioxide free distilled water. A dense white flocculent precipitate immediately forms. The suspension was stirred for a few minutes and filtered through a large Buchner funnel. The white precipitate of triphenyl lead hydroxide was washed with warm carbon dioxide free distilled water until a negative chloride ion test was obtained with silver nitrate. The residue was dried in a vacuum desiccator over solid sodium hydroxide. The yield was 4.28 g (0.0094 mole) or 94 per cent. (Found: C, 47.49; H, 3.63. Calc. for $C_{18}H_{16}OPb$: C, 47.43; H, 3.55%.) No melting was observed up to about 240°, above which partial liquifaction occurs.

Triphenyl lead azide. At room temperature (25°C), 3.87 g (0.0085 mole) of dry triphenyl lead hydroxide was placed in a one-necked 300 ml reaction flask which is equipped with a thermometer, and a dropping funnel (60 ml) with a gas equalizing side arm. Two hundred millilitres of absolute ethanol were added and partial solubility is achieved by employing a magnetic stirring assembly. After approximately one hour, 25 ml of absolute ethanol were placed in the funnel. A chloroform solution of hydrazoic acid(10) (0.00855 mole) was pipetted into the 25 ml of ethanol. The system was closed and the reaction mixture stirred vigorously while the hydrazoic acid solution was added over a 15 min addition time. The appearance of a white crystalline solid suspended in the reaction mixture was indicative of the presence of triphenyl lead azide. Care was taken that the temperature of the reaction mixture did not exceed 35°C. After 4 hr of stirring beyond addition time, the reaction mixture was transferred to a beaker containing 500 ml of carbon dioxide free distilled water. The ethanolic water suspension was stirred briefly and cooled to 0°C. The resulting suspension was filtered by suction using a large Buchner funnel. The resulting white crystalline mass was washed with 25 ml of cold aqueous ethanol (1 part ethanol–3 parts water). The residue was dried in a vacuum desiccator over solid sodium hydroxide. The yield of triphenyl lead azide was 3.92 g (0.00816 mole) or 96 per cent. (Found: C, 44.90; H, 3.21; N, 8.70. Calc. for $C_{18}H_{15}N_3Pb$: C, 44.98; H, 3.15; N, 8.75%.)

Triphenyl lead azide crystallizes from cold ethanolic solution of the reaction medium in the form of small transparent needles. While insoluble in water, it is soluble to the extent of 1.39 g per 100 ml of solution in 95 per cent ethanol and to 0.12 g per 100 ml of solution in anhydrous diethyl ether. The crystals exhibit acicular habit and birefringence. The index of refraction is about 1.6 for the long edge of the crystals.‡ The density of the crystals is 1.77 g cm^{-3} at 30°C. An X-ray diffraction powder pattern was obtained with CuKα was obtained employing a North American Philips unit and the d-spacings in Å were found to be: 15.41, 9.30, 7.96, 7.40, 6.42, 5.41, 5.25, 5.01, 4.84, 4.66, 4.30, 4.13, 4.07, 4.00, 3.85, 3.73, 3.61, 3.44, 3.37, 3.29, 3.10, 3.00, 2.87, 2.82, 2.77, 2.71, 2.67, 2.61, 2.56 and 2.49. The four strongest lines were 7.96, 7.40, 4.66 and 5.01, in the order of decreasing intensity. Triphenyl lead azide has no true melting point and decomposes on heating. Thus, a sample heated to 160° showed considerable loss of nitrogen.

Diphenyl lead dichloride.(7) Tetraphenyl lead was dissolved in benzene by warming to 50° (1 g per 10 ml of benzene) and vigorously stirring in an open reaction flask fitted with a gas inlet tube. The hydrogen chloride gas was introduced slowly. The precipitate of diphenyl lead dichloride was characterized by the appearance of small shiny white plates. The warm mixture was suction filtered through a hot stage (50°) filter. The filtrate was maintained at 50° and returned to the reaction flask for further treatment with hydrogen chloride. Successive treatments required a correspondingly shorter gas flow interval. When it was observed that the gas flow interval increased markedly, further treatment was not resumed. The precipitate from this treatment was found to contain a small amount of lead (II) chloride. The residue of diphenyl lead dichloride was washed with hot benzene and dried in a vacuum desiccator. The yield obtained from 10.3 g (0.0200 mole) of tetraphenyl lead was 8.25 g (0.0194 mole) or 97 per cent. (Found C, 33.39, H, 2.24, Cl, 16.55. Calc. for $C_{12}H_{10}ClPb$ C, 33.34, H, 2.33, Cl, 16.40%.) Diphenyl lead dichloride turns from white to yellow at 283–286° without melting.

---

* Microanalyses by Dr. C. WEILER and Dr. F. B. STRAUSS, Oxford, England.

† Unless otherwise specified, melting points are uncorrected and were determined on a Fisher Johns Melt Point Block at a heating rate of 4–5 degrees per minute.

‡ An AO Spence polarizing microscope was employed.

(9) G. GRÜTTNER, *Ber. Dtsch. Chem. Ges.* **51**, 1320 (1918).

(10) H. WOLFF, *Organic Reactions* **3**, 327 (1946).

Diphenyl lead oxide(11) To a hot suspension of 4.32 g (0.010 mole) of diphenyl lead dichloride in 300 ml of absolute ethanol, 20 ml of 10 per cent absolute ethanolic potassium hydroxide was slowly added under vigorous stirring. The reaction mixture was stirred an additional 30 min after addition was completed. The warm alcoholic suspension was filtered through fine grade filter paper in a heated funnel (65°C). The white residue was transferred to a mortar and pestle and triturated with hot ethyl alcohol (95 per cent). The hot suspension is refiltered through a heated funnel and the filtrate was tested for the presence of chloride ion with aqueous silver nitrate. The trituration was repeated if necessary. The residue was washed with small amounts of hot, carbon dioxide free distilled water and refiltered. The white amorphous residue was dried in a vacuum desiccator over solid sodium hydroxide. The yield was 3.40 g (0.0090 mole) or 90 per cent. (Found C, 38.16, H, 2.76. Calc. for $C_{12}H_{10}OPb$ C, 38.19, H, 2.67%.) On heating diphenyl lead oxide appears to decompose at 223°.

Diphenyl lead diazide To 3.02 g (0.0080 mole) of finely ground diphenyl lead oxide 200 ml of absolute ethyl alcohol was added in a one-necked 300 ml reaction flask at room temperature. The suspension was stirred vigorously for 1 hr to reduce the particle size of the suspended material. The flask was equipped with a dropping funnel with a gas equalizing arm. A chloroform solution of hydrazoic acid of sufficient titer to contain 0.723 g (0.0168 mole) of the acid was pipetted into 25 ml of absolute ethyl alcohol contained in the funnel. The suspension was stirred continuously by a magnetic stirrer while the hydrazoic acid solution was added over a 15 min interval. The appearance of white crystalline solid which is of very small particle size is indicative that the reaction is progressing. The suspension was stirred for an additional six hours after addition of the acid was completed. The mixture was filtered by suction and the resulting white crystalline mass was washed with ethanol. The residue was dried in a vacuum desiccator over solid sodium hydroxide. A yield of 3.45 g (0.0077 mole) or 97 per cent was obtained. (Found C, 32.61, H, 2.46, N, 18.62. Calc. for $C_{12}H_{10}N_6Pb$ C, 32.35, H, 2.26, N, 18.87%.)

Diphenyl lead diazide is obtained in the form of very small needle-like crystals from the reaction mixture. The crystals are birefringent and had an acicular habit. Diphenyl lead diazide is insoluble in water, 95 per cent ethanol and anhydrous diethyl ether. It has a density of 1.69 g cm^{-3} at 30°C. The *d* spacings in Å from the X-ray powder pattern are: 11.82, 6.75, 6.45, 5.97, 5.46, 4.95, 4.59, 4.35, 4.09, 3.99, 3.83, 3.74, 3.58, 3.42, 3.24, 3.19, 3.13, 2.96, 2.93 and 2.75. The strongest lines are 11.82, 6.75, 6.45, 3.99, 3.83 and 5.97 in the order of decreasing intensity. Diphenyl lead diazide has no melting point and decomposes on heating with gas evolution observed around 145°C.

Differential thermal analysis and simultaneous gas profile Differential thermal analysis of the two lead (IV) azides was carried out using nickel sample holders and chromel-alumel thermocouples a heating rate of about 9.5°C min^{-1}. Simultaneous gas profile was obtained by the method of Ayres(12).

Infra-red spectra Infra-red spectra of the two lead (IV) azides and their precursors were recorded on a Perkin-Elmer, Model 21, spectrometer and a Perkin-Elmer Model 137B spectrometer both fitted with rock salt optics. The samples were prepared as mineral oil mulls or potassium bromide pellets.

RESULTS AND DISCUSSION

Triphenyl lead azide (I) has been prepared starting from tetraphenyl lead by employing the following sequence of reactions

$$(C_6H_5)_4Pb + HCl \rightarrow (C_6H_5)_3PbCl + C_6H_6$$

$$(C_6H_5)_3PbCl + KOH \rightarrow (C_6H_5)_3POH + KCl$$

$$(C_6H_5)_3PbOH + HN_3 \rightarrow (C_6H_5)_3PbN + H_2O$$

L. Zechmeister and J. Csabay, *Ber. Dtsch. Chem. Ges.* **60**, 1617 (1927)

W. M. Ayres and E. M. Bens, *Analyt. Chem.* **33**, 569 (1961)

Diphenyl lead diazide (II) has been prepared by the following scheme of reactions

$$(C_6H_5)_4Pb + 2HCl \rightarrow (C_6H_5)_2PbCl_2 + 2C_6H_6$$

$$(C_6H_5)_2PbCl_2 + 2KOH \rightarrow (C_6H_5)_2PbO + 2KCl + H_2O$$

$$(C_6H_5)_2PbO + 2HN_3 \rightarrow (C_6H_5)_2Pb(N_3)_2 + H_2O$$

Triphenyl lead azide shows no explosive properties but rather ignites quitely It burns with a bright yellow flame depositing metallic lead Triphenyl lead azide does not show a sharp melting point and decomposes slowly on heating When crystals were observed under a hot-state polarizing microscope, loss of birefringence was noticed at 159 164°C Decomposition of triphenyl lead azide in air first gives rise to a brown lead oxide (probably PbO_2) which on further heating turns black around 290°C The formation of the yellow lead oxides (PbO, Pb_2O_3) was observed around 190°C There was evidence for the formation of some polyphenyl compounds produced by the recombination of phenyl radicals These compounds have not yet been characterized * Mass spectrometric analysis of the gas evolved by the decomposition of triphenyl lead azide in the temperature range 26 200°C showed 88 per cent nitrogen and 12 per cent benzene Differential thermal analysis of triphenyl lead azide showed a sharp endothermic reaction peak around 190°C A gas profile obtained simultaneously showed large gas evolution, probably of nitrogen Slow decomposition was however, observed even at lower temperatures Exothermic peaks were found in the region 200 300°C, probably due to radical recombination reactions and transformations of lead oxides *

Diphenyl lead diazide (II) on heating decomposes without melting In this case also, there was evidence for the formation of polyphenyl compounds * The thermal study of diphenyl lead diazide in a manometric apparatus was initially accompanied by a violent explosion in the region of 190 200°C destroying the apparatus Subsequently, successful thermal manometric runs were obtained by diluting the sample with finely divided Ottawa Sand Mass spectrometric analysis of the gas showed 77 9 per cent nitrogen, 10 7 per cent carbon dioxide, 3 6 per cent hydrazoic acid and 7 4 per cent of benzene The differential thermal analysis of diphenyl lead diazide showed an endothermic peak around 190°C associated with gas evolution as indicated by the simultaneous gas profile Exothermic reactions were observed in the 270 330°C region probably due to radical recombination and transformations of the lead oxides * The formation of brown and black lead oxides was observed during the decomposition just as in the case of triphenyl lead azide

From these studies it becomes obvious that the phenyl lead (IV) azides are highly stable as compared to the explosive lead (II) azide This is probably associated with the greater covalent character of the Pb-N bond in the phenyl lead (IV) azides It is interesting to note the effect of the number of phenyl groups on the stability of these azides Triphenyl lead azide is considerably more stable than diphenyl lead diazide Presumably, phenyl lead triazide (III) should prove to be much less stable than

$$\underset{III}{C_6H_5Pb(N_3)_3}$$

diphenyl lead diazide †

---

* Detailed studies on this aspect are presently in progress

† Detailed studies of this aspect are currently in progress

The infra-red absorption spectra of the two phenyl lead (IV) azides and their precursors show relatively intense bands due to aromatic ring vibrations caused by the activation of the heavy lead atom.(13) Some of these bands, as well as the C—H out-of-plane deformation bands appear at considerably low frequencies due to the mass effects of the lead atom.(13) The two phenyl lead (IV) azides show the characteristic and symmetric stretching frequencies of the azido group(14,15) around 2040 and 1280 cm^{-1}, respectively, when the spectra are recorded in Nujol mull. The azide bending mode gives rise to a weak band around 650 cm^{-1}. When the spectra of the two azides were recorded in potassium bromide pellets, the asymmetric stretching band was seen as a doublet ($\sim$2040 and 2120 cm^{-1}). It was first considered that the splitting could be due to an ion displacement reaction with the matrix.(16) Since the new band, around 2120 cm^{-1}, is much higher than the characteristic frequency of potassium azide(15) (2040 cm^{-1}), the displacement reaction seems unlikely. The more plausible explanation appears to be recrystallization of the phenyl lead (IV) azide during grinding and pelleting. Such solid state anomalies are known to occur during preparation of pellets.(17,18,19) If the two phenyl lead (IV) azides recrystallize into forms of lower symmetry one would expect such band splittings. Thus, barium azide (monoclinic crystal structure) shows the asymmetric stretching band of the azide as a doublet.(15)

(13) C. N. R. Rao, J. Ramachandran and A. Balasubramanian, *Canad. J. Chem.* **39**, 171 (1961).

(14) E. Lieber, C. N. R. Rao, T. S. Chao and C. W. W. Hoffman, *Analyt. Chem.* **29**, 916 (1957).

(15) P. Gray and T. C. Waddington, *Trans. Faraday Soc.* **53**, 901 (1957).

(16) V. M. Meloche and G. E. Kalbus, *J. Inorg. Nucl. Chem.* **6**, 104 (1958).

(17) A. W. Baker, *J. Phys. Chem.* **61**, 450 (1957).

(18) E. Smakula, A. Gori and H. Wotiz, *Spectrochim. Acta* **9**, 346 (1957).

(19) A. Tolk, *Spectrochim. Acta* **17**, 511 (1961).

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 637 to 640. Pergamon Press Ltd. Printed in Northern Ireland

TRIPHENYLPHOSPHINE OXIDE COMPLEXES OF NON-TRANSITION METAL HALIDES

M. J. Frazer, W. Gerrard and R. Twaits
The Northern Polytechnic, London N.7

(*Received 2 August 1962, in revised form 1 October 1962*)

Abstract—The triphenylphosphine oxide (TPO) complexes with transition metal halides have been investigated extensively over the last few years,[1–3] but the only complexes with non-transition metal halides previously mentioned are 2TPO.$ZnCl_2$,[4] 2TPO.ZnI_2,[4,5] 2TPO.CdI_2,[4,5] 2TPO.$HgCl_2$,[4,5] 2TPO.$SnCl_4$,[3] 2TPO.$SnBr_4$[3] and TPO.$SbCl_5$.[6] Our purpose was to prepare a number of complexes of non-transition elements with TPO, and to attempt to correlate the decrease, $\Delta\nu$, in the phosphoryl stretching frequency on complex formation with the nature of the acceptor molecule. Details of twenty new complexes are given in the Table 1. We also prepared many transition metal halide complexes; of these, 2TPO.$FeCl_2$, 2TPO.$FeCl_3$ and 3TPO.$CrCl_3$, have not been reported elsewhere and are included in the Table.

EXPERIMENTAL

Preparation of the complexes. The complexes were prepared by dissolving the halide or its hydrate and TPO in appropriate proportions in one of the solvents (see Table) usually under reflux. On cooling or evaporating the solvent, the complex was precipitated and was then recrystallized.

Infra-red Spectra. As this work was intended only as a preliminary survey a Perkin-Elmer Model 137 (Infracord) was used, and consequently the frequency values are only accurate to about ±4 cm^{-1}. The spectra were taken in nujol mulls. The phosphoryl frequency for pure TPO as nujol mull or in methylene chloride solution was found at 1190 cm^{-1}, in agreement with the results of Daasch and Smith[7] and Hallman and Pinkas[8], but other reported values are 1180,[3] 1186[1] and 1195 cm^{-1}.[5]

Action of heat on the TPO.PCl_5 complex. The complex (9.05 g) was heated at 200°C at 20 mm Hg for 4 hr. A −80°C trap condensate was phosphoryl chloride (77 per cent) and the residue was triphenylphosphorus dichloride (60 per cent), (Found: Cl, 21.8. Calc. for $C_{18}H_{15}Cl_2P$: Cl, 21.3%.)

DISCUSSION

The decrease in the phosphoryl stretching frequency on complex formation has been discussed by Cotton *et al.*[5] These authors consider that the decrease of $p_\pi \rightarrow d_\pi$ back bonding from O to P overcomes effects such as enhanced P—O σ-bonding and metal–oxygen π interaction, which would increase the bond order and hence the phosphoryl stretching frequency. The main effect thus appears to be the polarisation of the PO bond, and this must be related to the strength of the metal–oxygen bond. We therefore considered that it might be possible to correlate the decrease in the phosphoryl stretching frequency, $\Delta\nu$, with the Lewis acid strength of the metal halide

---

[1] For leading reference see F. A. Cotton and D. M. L. Goodgame *J. Chem. Soc.* 3735 (1961).

[2] For leading reference see Von K. Issleib and B. Mitscherling, *Z. Anorg. Chem.* **304**, 73 (1960).

[3] J. C. Sheldon and S. Y. Tyree *J. Amer. Chem. Soc.* **80**, 4775 (1958).

[4] R. H. Pickard and J. Kenyon *J. Chem. Soc.* 262 (1906).

[5] F. A. Cotton, R. Barnes and R. Bannister *J. Chem. Soc.* 2199 (1960).

[6] I. Lindqvist and G. Olofsson, *Acta Chem. Scand.* **13**, 1753 (1959).

[7] L. W. Daasch and D. C. Smith *Analyt. Chem.* **23**, 853 (1951).

[8] M. Halman and S. Pinkas, *J. Chem. Soc.* 3264 (1958).

TABLE 1 COMPLEXES OF TRIPHENYLPHOSPHINE OXIDE

Complex	Solvent used in Preparation	Colour	m p (°C)	Found Requires M	X	$\Delta\nu \pm 8$ cm^{-1} cm^{-1}
TPO MgCl$_2$	*c*	White	249	6.6	18.8	26
				6.5	19.0	
2TPO ZnBr$_2$	*a*	White	230	8.5	20.8	−39
				8.4	20.5	
2TPO CdCl$_2$	*b*	White	173	15.5	9.7	−14
				15.2	9.6	
2TPO CdBr	*a*	White	207	13.7	19.6	35 av
				13.6	19.3	
2TPO HgBr$_2$	*a*	White	128	21.8	16.2	−34 av
				21.9	17.4	
2TPO HgI$_2$	*b*	White	118	19.5	24.9	−36 av
				19.8	25.1	
TPO BF$_3$	*c*	White	239	8.4*	—	—
				8.9	–	
TPO BBr$_3$	*d*	Cream	140–150	2.1	45.0	−103
				2.0	45.3	
TPO AlCl$_3$	*c*	White	157	6.4	25.4	35
				6.5	25.8	
TPO GaCl$_3$	*c*	White	150	14.3	23.4	34 av
				15.3	23.4	
2TPO InCl$_3$	*a*	White	256	14.9	13.7	−34 av
				14.8	13.7	
2TPO TlCl$_3$	*a*	White	199	23.6	12.0	−33 av
				23.6	12.3	
2TPO SiCl$_4$	*f*	White	146–150	3.9	19.1	31 av
				3.9	19.5	
2TPO SnI$_4$	*b*	Brown	206–208	10.8	42.6	43 av
				10.0	42.9	
2TPO AsCl$_3$	*d*	White	decomp	10.5	14.6	−36
				10.2	14.4	
2TPO SbCl$_3$	*b*	White	169	16.3	13.5	63 to 90
				15.5	13.6	
2TPO BiCl$_3$	*b*	White	222	24.1	11.8	40
				24.0	12.2	
2TPO BiBr$_3$	*b*	Cream	179	21.2	23.9	46
				20.8	23.8	
2TPO BiI$_3$	*b*	Orange	201	18.6	32.9	−51
				18.2	33.2	
TPO PCl$_5$	*d*	Cream	135–140	5.9	36.4	—
				6.4	36.4	
2TPO FeCl$_2$	*b*†	Brown	decomp	8.6	10.8	−42
				8.2	10.4	
2TPO FeCl$_3$	*a*	Yellow	183	7.9	14.8	−43
				7.8	14.8	
3TPO CrCl$_3$	*a*	Puple	252–253	5.3	10.8	−34
				5.2	10.7	

a, ethyl alcohol, *b*, acetone, *c*, diethyl ether, *d*, carbon tetrachloride, *e*, xylene, *f*, benzene
† under N$_2$ * analysis is for P av = average value

Related work on ethyl acetate–metal halide complexes,[(9)] has indicated that there is a correlation between the shift in the carbonyl frequency and the Lewis acid strength of the acceptor molecule. Kinell *et al.*[(10)] have stated that the use of $\Delta\nu$ as an indication of electron acceptor strength is permissible only "if the acceptor molecules to be compared are under very similar conditions", and this point was illustrated later by Alden and Zackrisson[(11)], who found that $Me_3PO \cdot SbCl_3$ and $Me_3PO \cdot SbCl_5$ had similar $\Delta\nu$'s but quite different enthalpies of formation. We now survey a number of TPO–metal halide complexes and for a series of similar complexes, the order of $\Delta\nu$ values are taken as the order of Lewis acid strengths of the metal halides with respect to TPO as reference base.

Interpretation of the spectra in this way is sometimes made difficult by the splitting of the shifted phosphoryl band. Splitting may be due to the coupling of PO vibrations via the metal atom, or to the existence of non-equivalent ligands in the crystal. Following the practice of Cotton *et al.*,[(5)] when the band is split the average value is given (marked av.).

Group II complexes. The series of compounds, $2TPO \cdot MX_2$, where M = Zn, Cd, Hg and X = Cl, Br and I is now complete. For the previously reported compounds the shifts (cm^{-1}) are −37 for $2TPO \cdot ZnCl_2$, −41(−44[(5)]) for $2TPO \cdot ZnI_2$, −36 (−42[(5)]) for $2TPO \cdot CdI_2$ and −27(−25[(6)]) for $2TPO \cdot HgI_2$, the values in brackets are those given originally. For each metal there is a slight increase in $\Delta\nu$ in the order I < Br < Cl. The melting points of the three zinc halide adducts are 229, 230 and 231°C, and it is of interest that we find melting points in the range 227–233° for the two other groups of complexes, of this type, which are expected to have undistorted tetrahedral structures, i.e. those with M = Mn(II) (d^5) and Co(II) (d^7).

Group III complexes. $TPO \cdot BCl_3$ has been reported previously[(12)] with $\Delta\nu$ = −117 cm^{-1}. The values for the complexes $TPO \cdot MCl_3$ are in the order B > Al ~ Ga. Indium and thallium trichlorides form 2 : 1 complexes and so cannot be included in this series. With ethyl acetate as reference base Lappert[(9)] finds the order B > Ga > Al > In.

It is not possible to give $\Delta\nu$ for the boron trifluoride adduct, because bands attributed to boron–fluorine stretching occur in the 8–9 μ region. The boron tribromide complex has $\Delta\nu$ = −103 cm^{-1}, which is less than that for the trichloride. Previous indications are that boron tribromide is a stronger acceptor than boron trichloride with respect to ethyl acetate,[(9)] pyridine[(13, 14)] and trimethylamine.[(14)]

Group IV complexes. Sheldon and Tyree[(3)] have prepared the compounds $2TPO \cdot TiCl_4$, $2TPO \cdot SnCl_4$ and $2TPO \cdot SnBr_4$. Their values which refer to the "maximum in the proposed PO absorption band" are −50, −55 and −55 cm^{-1} respectively. For the same compounds, with good analysis, we have $\Delta\nu$ as −42, −42 and −44 cm^{-1}, but these figures represent the average for the split band. $2TPO \cdot SiCl_4$ and $2TPO \cdot SnI_4$ have now been prepared. The shifts for the chlorides are Sn ~ Ti > Si and for the tin compounds Cl ~ Br ~ I. Lappert[(9)] summarizing his own and earlier results

---

M. F. Lappert, *J. Chem. Soc.* 542 (1962).

P. Kinell, I. Lindqvist and M. Zackrisson, *Acta Chem. Scand.* **13**, 1159 (1959).

K. I. Alden and M. Zackrisson, *Acta Chem. Scand.* **14**, 994 (1960).

M. J. Frazer, W. Gerrard and J. K. Patel, *J. Chem. Soc.* 726 (1960).

C. M. Bax, A. R. Katritzky and L. E. Sutton, *J. Chem. Soc.* 1258 (1958).

H. C. Brown and R. R. Holmes, *J. Amer. Chem. Soc.* **78**, 2173 (1956); N. N. Greenwood and P. G. Perkins, *J. Chem. Soc.* 1141 (1960).

gives the order of acceptor strengths of the halides in this group as Ti ~ Sn Ge Si and for tin Cl Br

Group V complexes The compounds 2TPO MCl$_3$ exhibit shifts in the order Sb Bi As and for 2TPO BiX$_3$ the order is I Br Cl

The white solid formed when TPO is added to phosphorus pentachloride is probably not a simple adduct Evidence that it is more likely a 1 1 complex, Ph$_3$PCl$_2$ POCl$_3$, is that (i) there is no absorption in the 8 4 8 9 μ region, where a shifted PO band could reasonably be expected, (ii) the infra-red spectrum is identical to that of a 1 1 mixture of triphenylphosphorus dichloride and phosphoryl chloride, and (iii) these two compounds are obtained when the solid is heated Triphenylphosphorus dichloride has indeed been prepared from TPO and phosphorus pentachloride(15) and a similar reaction occurs with triethylphosphine oxide(16) Recently HORNER and TYREE(17) have likewise found that molybdenum (V) chloride abstracts oxygen from TPO to give the complexes 2TPO MoOCl$_3$ and 2TPO MoO$_2$Cl$_2$ The compound formed from antimony (V) chloride and TPO(6) may also be more complicated than a simple 1 1 adduct, but no infra-red spectral details were given

Acknowledgement - The authors thank Dr F F MOONEY and M GOLDSTEIN for assistance with the infra-red spectra

(15) V GRIGNARD and J SAVARD *C R Acad Sci*, *Paris* **192** 592 (1931)
(16) J N COLLIE and J REYNOLDS, *J Chem Soc* 367 (1915)
(17) S M HORNER and S Y TYREE, *Inorg Chem* **1**, 122 (1962)

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 641 to 656. Pergamon Press Ltd. Printed in Northern Ireland

KINETICS OF THE REACTION OF HYDROGEN WITH ZIRCONIUM–TITANIUM ALLOY

V. Y. Labaton,* S. G. Donn,† R. H. Watson† and E. Whitehead†
United Kingdom Atomic Energy Authority (Reactor Group)
Reactor Technology Branch, Capenhurst, Chester

(*Received* 18 *December* 1961, *in revised form* 2 *October* 1962)

Abstract—The rate of reaction between zirconium–titanium alloys, containing 50 and 55 atomic per cent zirconium and hydrogen, has been studied under static and flow conditions. It has been shown that under most conditions studied the reaction is first order. The effect of surface state and of impurities in the hydrogen on the reaction have been investigated. For comparable static and flow experiments at 550°C the reaction rates determined were 2×10^{-6} g/cm² min mmHg and 0.5×10^{-6} g/cm² min mm Hg respectively. The calculated activation energies for the reaction are 4.1 kcal/mole between 400 and 520°C and 15.7 kcal/mole between 520 and 600°C. A brief comparative study with unalloyed zirconium showed the reaction to be first order and gave an activation energy of 17.3 kcal/mole between 400 and 470°C.

THIS investigation was initiated to provide basic data for the design of a "gettering" system for the removal of hydrogen from an inert gas stream. It was later extended to elucidate the fundamentals of the kinetics of the reaction. The work was closely integrated with related phase and equilibrium pressure studies of the system.[1]

The kinetics of the zirconium–hydrogen reaction have been studied by GULBRANSEN and ANDREW. In their initial study,[2] they concluded that the reaction rate was proportional to the square root of the hydrogen pressure. These results have since been interpreted[3] in terms of an oxide-contaminated surface and the reaction is now believed to be diffusion-controlled.

GULBRANSEN and ANDREW[4] obtained similar kinetic results for the titanium–hydrogen system to those originally obtained for the zirconium–hydrogen system, the reaction rate being proportional to the square root of gas pressure. These results have since been interpreted by MORTON[5] in terms of a reaction controlled by a surface oxide film. MORTON's investigation showed that the reaction was first-order with respect to hydrogen pressure or the amount of hydrogen absorbed, but he concluded that the absorption rate was controlled by a surface oxide film in his experiments as in those of GULBRANSEN and ANDREW.

The present study included static experiments with varying and constant hydrogen pressure above the metal and flow experiments through beds packed with divided metal. The static experiments were devised to provide information on equilibrium pressures of hydrides and rates of reaction in pure hydrogen, the flow experiments were made to obtain reaction rates in a system more analogous to a gettering system, with a flowing inert carrier gas containing a trace of hydrogen The effect of surface pretreatment on reactivity was investigated

---

* Present Address: U.K.A.E.A. (Reactor Group), Risley, Warrington, Lancashire.

† Present Address: U.K.A.E.A. (Production Group), Springfields, Salwick, Lancashire.

[1] R. PASCARD and R. FABRE, *Symposium 'Glove Boxes and Shielded Cells'* Paper 15 (1957). Butterworths, London (1958).

[2] E. A. GULBRANSEN and K. F. ANDREW, *Trans. Amer. Inst. Engrs.* **185,** 515 (1949).

[3] E. A. GULBRANSEN and K. F. ANDREW, *Rev. Metall.* **51,** 101 (1954).

[4] E. A. GULBRANSEN and K. F. ANDREW, *Trans. Amer. Inst. Engrs.* **185,** 741 (1949).

[5] P. H. MORTON, Imperial Chemical Industries, Ltd. Private communication (1956).

THEORETICAL ASPECTS OF THE REACTION KINETICS

The reaction between metal and hydrogen may be taken to follow the equation

$$\frac{dw}{dt} = kAP^n$$

where dw/dt = rate of hydrogen absorption, g/min, k = rate constant for the hydrogen-metal reaction g/cm² min (mm Hg)^n A = area of sample, cm², P = pressure of hydrogen (mm Hg) n = index or order of reaction

Constant-volume system

In a constant-volume system of V cm³ at T K,

$$-\frac{V}{RT}\frac{dP}{dt} = kAP^n$$

where R = gas constant mm Hg cm³/g deg K

$$\text{i e} \quad \frac{dP}{dt} = -\frac{kART}{V}P^n \qquad (1)$$

If n = 1 0 equation (1) can be integrated to give

$$\ln P - \ln P_0 = -Kt \qquad (2)$$

where

$$P_0 = \text{initial pressure (mm Hg)}$$

$$\text{and } K = \frac{kART}{V}\ \text{min}^{-1}$$

The equilibrium pressure of hydrogen, P_E, above the "hydride" phase increases with the hydrogen content When the hydride composition is high enough to make P_E of comparable magnitude to P, the equation applied to the reaction is

$$\frac{\delta(P - P_E)}{\delta t} = \frac{kART}{V}(P - P_E)^n \qquad (3)$$

since $(P - P_E)$ is the driving force When n = 1 0, this can be integrated to give

$$\ln(P - P_E) - \ln P_0 = -Kt \qquad (4)$$

where P_E is a function of $(P_0 - P)$ and the sample weight

This function is not explicit, and values of P_E corresponding with values of $(P_0 - P)$ can be obtained by calculation of the hydride compositions and experimental determination of the equilibrium hydrogen pressure

Constant pressure system

In a constant pressure system, if the reaction is carried out at a series of pressures then a plot of ln (rate of reaction) against ln P will give a straight line of slope n

and intercept ln K. In apparatus of the type used, the rate of reaction can be expressed in terms of dP/dt or $d(P - P_E)/dt$ (as appropriate), the rate of change of pressure in the "supply part" of the apparatus, which is of constant volume.

Flow system

An element of a bed packed with divided metal is considered with free space dV and metal surface area dA. In this case, P is the partial pressure of hydrogen in the inert gas stream. If $n = 1.0$, then

$$\frac{dP}{dt} = -\frac{kdART}{dV} P = -KP$$

If the bed is uniformly packed, $dA/dV = A/V$, and if F is the flow rate of carrier gas, $dt = dV/F$, hence

$$\frac{dP}{dV} = -\frac{K}{F} P$$

This can be integrated to give

$$\ln \frac{P_1}{P_0} = -\frac{KV}{F}$$

Since the concentration of hydrogen in inert carrier gas is proportional to its partial pressure,

$$\ln \frac{C}{C_0} = -\frac{KV}{F}$$

When the equilibrium pressure is taken into account,

$$\ln \left(\frac{C - C_E}{C_0}\right) = -\frac{KV}{F}$$

Thus, if the reaction is unit order, then if F is varied and values of C (the outlet concentration) are measured, a straight line through the origin will be obtained if $\ln [C_0/(C - C_E)]$ is plotted against V/F (the residence time of the gas in the packed bed). The slope of the line gives

$$K = \frac{kART}{V} \text{ min}^{-1}$$

EXPERIMENTAL

Preparation of materials

The 50 atomic per cent zirconium-titanium alloy was prepared in the form of buttons from iodide zirconium and high-grade titanium sponge. Turnings, of average thickness 0.01 in, were made from the buttons under argon and stored under the same gas. Strips (analysis showed Ti, 35.1 Hf, 2.0, O 0.09 wt%) of average thickness 0.05 in., was made by hot-rolling the buttons in a mild-steel sheath followed by a final cold roll unsheathed.

The 55 atomic per cent zirconium titanium alloy was obtained from Imperial Chemical Industries Limited (Metals Division)[6] as ingot. Turnings, of average thickness 0.01 in., were initially prepared from the ingot by machining in air and subsequently storing under argon, their oxygen content was found to be 0.14 wt%. Discs of this alloy, of thickness 0.06 in., were also cut in air from the ingot. Later, turnings were cut under oil and stored under degassed kerosene, their oxygen content was 0.07 wt%. (Analysis of the turnings showed Ti, 30.4, Hf, 1.4 wt%.)

Reaction with hydrogen at varying pressure under static conditions

Specimens contained in a silica tube were exposed to a given pressure of hydrogen in a calibrated constant-volume system and the variation of pressure with time was followed by observing a manometer with a cathetometer The volume of the reaction space was 1540 cm^3 and, in comparison with this the 15 cm^3 volume of the heated reaction tube containing the alloy sample could be neglected The percentage errors introduced by variations in ambient temperature were not considered large enough to justify thermostatting the apparatus The temperature of the reaction tube was measured by a Pt 13% Rh Pt thermocouple the e m f of which was fed into a control system which could hold the temperature automatically within 3 C of a chosen value

A typical analysis of the electrolytic grade hydrogen used was (in vol %) H_2 99.82, O_2, 0.02, N_2 0.12, CO_2 0.06 CO 0.02 CH_4 0.002

Reaction with hydrogen at constant pressure under static conditions

The apparatus, previously described,(6) consisted of two sections connected by a pressure regulating valve The sample in a silica tube was heated under a constant pressure of hydrogen in one section, and as reaction proceeded hydrogen was admitted through the regulating valve from a storage section of known volume The rate of uptake of hydrogen by the sample was followed by the decrease of hydrogen pressure in the storage section The sample was heated in a furnace controlled to 3 C by a Kent Multilec control system

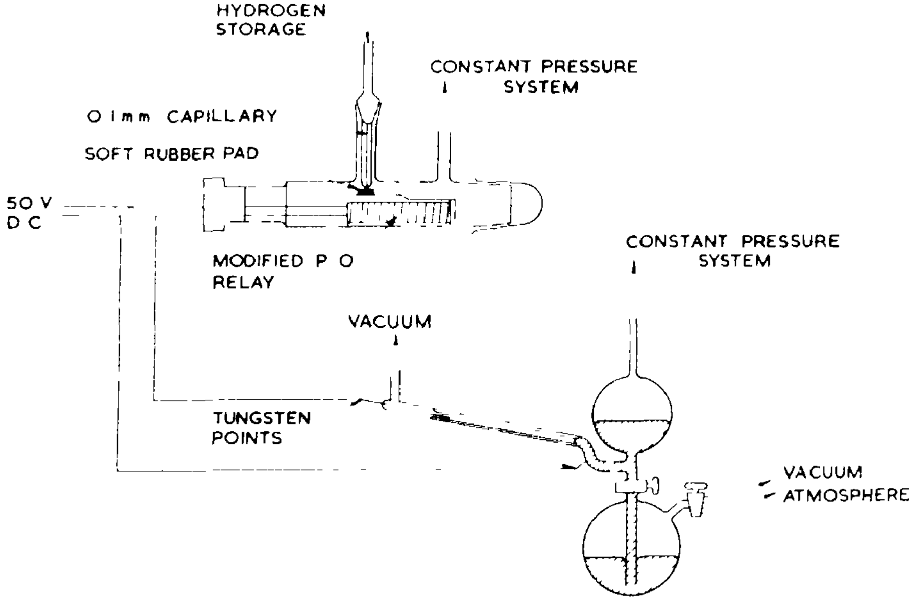


FIG 1 – Constant pressure regulating device

The pressure regulating valve consisted of a soft rubber pad seating on a glass capillary inlet and was actuated by a modified Post Office relay,(7) as shown in Fig 1 This relay was operated by a mercury switch, and the pressure of hydrogen above the alloy sample was held to ± 0.005 mm Hg The hydrogen used was of electrolytic purity

After sufficient points had been obtained at one pressure, the hydrogen was removed from the sample by heating to 850 C and pumping down to an isolation pressure of 0.05 μ The reaction was then repeated at the same temperature with a different pressure of hydrogen

(6) V Y LABATON E V GARNER and E WHITEHEAD, *J Inorg Nucl Chem*, **24,** 1197 (1962)

(7) G W JACOBS, *Industr Engng Chem* (Analyt) 7, 70 (1935)

Reaction with hydrogen under flow conditions in packed beds

Argon containing 1000 parts per million by volume of hydrogen was passed through a packed bed of zirconium titanium turnings at the desired temperature, and the hydrogen concentration in the gas leaving the bed was measured

The argon from a cylinder was purified by passing it first through Linde molecular sieve type 5A (at ambient temperture) to remove water vapour, and then through a furnace containing calcium at 670 C to remove traces of oxygen and nitrogen The resulting gas contained between 5 and 10 p p m of water and less than 5 p p m of oxygen

The hydrogen was produced electrolytically, and thus was saturated with water Gross amounts of water were removed in a cold trap at liquid-nitrogen temperature Traces of oxygen were taken from the hydrogen by catalytic reduction on platinized asbestos at 300 C, the water so produced being absorbed by phosphorous pentoxide Final drying to the level of a few p p m was achieved by passing the hydrogen through a second cold trap immersed in liquid nitrogen, and then through a bed of Linde molecular sieve at ambient temperature

The two streams of pure gases were metered by capillary flow-meters in the ratio of 1000 1 of argon and hydrogen After joining, the gases passed through a mixer which created turbulence in the streams to ensure uniform composition From the mixer the gases entered the packed bed of zirconium-titanium alloy in the constant-temperature zone of the furnace, the temperature of which was controlled to ±1 5 C by a Sunvic energy regulator

Hydrogen in the outlet gas stream was measured by converting it to water in a bed of copper oxide pellets at 600 C, and then measuring the water content of the gas by a Dobson frost-point hygrometer Frost points could be determined with an accuracy of 0 5 C Since the frost-point hygrometer measured the total amount of water in the gas stream, two readings were necessary to measure the hydrogen content of the gas one when the gas stream by-passed the copper oxide bed, to determine the amount of water in the gas (usually 10 p p m), and the other when the gas stream passed through the oxidizer, to determine total water including that produced from the hydrogen The difference between the two readings gave the hydrogen content of the argon stream

At any particular temperature, the outlet hydrogen concentration was measured at varying flow rates, i e , at varying residence or reaction times in the bed As the equilibrium pressure of the hydride increases with increase in hydrogen content, this pressure had to be measured by passing argon containing no hydrogen over the zirconium-titanium as soon as possible after taking measurements at any particular flow rate and determining the hydrogen content of the stream leaving the bed The equilibrium pressure so measured was not the true equilibrium pressure for the system with a mean composition corresponding with the amount of hydrogen absorbed, it was a little larger than this, because of the increased hydrogen concentration at the surface of the alloy, and this changed with time as the hydrogen diffused into the lattice Thus, the equilibrium pressure had to be measured as soon as possible (usually 10 20 min) after the flow of hydrogen had ceased The difference between the measured and true equilibrium pressures was usually approximately 10–20 per cent

In the first series of runs (I) 23 1 g of 50 atomic per cent zirconium titanium alloy were packed in a length of 27 cm in a 3 5 cm-dia silica tube In the second series of runs (II), 53 4 g of 50 atomic per cent zirconium titanium alloy were contained in 23 cm of a tube 3 0 cm in diameter such that the packing density of the material was increased by a factor of 3 9 The third and fourth series of runs (III and IV) were made with 55 atomic per cent zirconium titanium alloy instead of the previously-used 50 atomic per cent alloy, in both these series of runs approximately the same weight of alloy about 58 g was packed into 22 cm of a tube 3 3 cm in diameter so that they had approximately the same packing density and bed volume The difference between the two series of runs was that the alloy for series III had been turned in air, whereas that for series IV had been turned under oil and stored under degassed paraffin

ctivity of the specimens and the effect of pretreatment

The treatment of each specimen before reaction is summarized below for the three types of ion study

Reaction with hydrogen at varying pressure under static conditions

(i) After degreasing in chloroform, the specimen was degassed at room temperature for at least 2 hr and generally overnight to a pressure of 0 05 μ Hg

(ii) A leak test was performed which gave a leak of 0.05 μ Hg over half an hour.
(iii) The specimen was heated at the reaction temperature for 2 hr while pumping was continued.
In some cases the specimens were pickled in a mixture containing 400 ml 14N HNO_3, 75 ml 40% HF and 525 ml H_2O, abraded under kerosene, or heated *in vacuo* to 1050°C.

(b) *Reaction with hydrogen at constant pressure under static conditions*
(i) After degreasing the specimen was degassed to a background pressure of 0.05 μ Hg at room temperature.
(ii) A leak test was performed which gave a leak of 0.05 μ over half an hour.
(iii) The specimen was heated at the reaction temperature for 15–30 min while pumping was continued.
In some cases the specimens were pickled or abraded before (i).

(c) *Reaction with hydrogen under flow conditions*
(i) The specimen was degassed at room temperature to 0.1 μ Hg.
(ii) The specimen was further degassed at 1050°C to an isolation pressure of 0.1 μ Hg. This operation took 5–10 hr, depending on the size of the bed. When fully degassed the alloy was blanketed with argon and cooled to the desired reaction temperature.
(iii) When the reaction was completed it was not practicable to remove each specimen, and the packed bed of metal was reactivated by pumping off the absorbed hydrogen at 1050°C to an isolation pressure of 0.1 μ Hg. This also dissolved any surface oxide layer. When not in use the bed was blanketed with argon.

The main aim in the pretreatment of the specimen was to produce a clean surface with minimum oxide coverage, and to preserve this by producing a good vacuum before bringing the specimen up to reaction temperature. HALL *et al.*,(8) when studying the reaction of zirconium and hydrogen found that the surface oxide film could be dissolved by heating to 1050°C.

Preliminary experiments indicated difficulty in reproducibility, the reaction rate depending on the rate of cooling down from 1050°C to the reaction temperature. Many times in the static rigs the sample failed to react initially, and the kinetic experiment had to be abandoned.

Any slight leak in the vacuum system greatly inhibits the reaction, and, depending on the size of the leak, the sample varied in colour from matt grey to shiny black, presumably because of different thicknesses of oxide film. In some experiments a black deposit of zirconium dioxide was formed on the reaction tube, this was attributed to the distillation of traces of metal halide on to the tube wall followed by decomposition and oxidation.

Abrasion to remove the oxide film was not necessary except in the case of 55 atomic per cent alloy, which was made by turning in air. Heating this to 1050°C was not sufficient to dissolve the oxide appreciably and to produce a reasonable reaction rate. Pickling of the alloy was not found to be very effective in removing the oxide film. However, pickling does not inhibit reaction, and this technique was used to produce thin samples of alloy.

Often where the pretreatment and reaction conditions of two identical samples were apparently the same, one would react and the other not. It is suggested that a possible reason for samples not reacting is the occurrence of undetected leaks during the period of heating to reaction temperature. No cases of non-reaction were observed in the dynamic experiments, where the ratio of metal to available oxygen was large.

Surface area measurements

The surface area of alloy swarf was determined by a gas permeability method, developed by KOZENY(9) and CARMAN,(10,11,12) in which the pressure drop across a packed bed was measured with gas flowing through it. From experiments with 50 atomic per cent swarf with a voidage of 0.80 a specific surface area of 60 cm^2/g was calculated (assuming a value of 5.0 for the dimensionless constant

---

(8) M. N. A. HALL, S. L. A. MARTIN and A. L. G. REES, *Trans. Faraday Soc.* **15**, 306 (1945).

(9) J. KOZENY, *Ber. Wein. Akad.* **136** A, 271 (1927).

(10) P. C. CARMAN, *Trans. Instn. Chem. Engrs. Lond.* **23**, 150 (1937).

(11) P. C. CARMAN, *J. Soc. Chem. Industr., Lond.* **57**, 225 (1938).

(12) P. C. CARMAN, *J. Soc. Chem. Industr., Lond.* **58**, 1 (1938).

B in the KOZENY-CARMAN equation). This value was used in the comparison of the rate constants obtained from static and dynamic experiments. The surface area estimated by geometrical measurement was about 6.0 cm²/g.

DISCUSSION OF RESULTS

Reaction at varying pressure under static conditions

Most of the kinetic measurements under these conditions were made at 550 °C. This temperature was chosen as a result of preliminary experiments on 50 atomic per cent alloy, and a consideration of the requirements of the gettering system. At 550 °C it was found that a reasonably rapid rate of reaction and a high concentration of hydrogen in the alloy were obtained with a "low" equilibrium pressure of hydrogen above the alloy.

Experiments in which P P_F. Two experiments were carried out with large samples of 55 atomic per cent alloy, so that several successive additions of hydrogen could be made to the sample while the equilibrium pressure remained negligible. The results of one experiment are plotted in Fig. 2. The maximum composition reached was (ZrTi) $H_{0.1}$, which at 550 °C corresponds with an equilibrium pressure of 9×10^{-2} mm Hg.

All the additions except one gave a linear plot of log pressure against time, indicating that the reaction is first-order. The lack of curvature in the lines indicated that any surface deactivation effect is negligible while the reaction is proceeding. A gradual change in slope between succeeding additions showed that some deactivation occurs at the end of each addition when the rate of hydrogen uptake is small. The change in slope was most pronounced when the sample had been left over-night (under the equilibrium pressure of hydrogen). In the fourth addition illustrated in Fig. 2 the line was no longer straight and the rate of reaction was greatly reduced. This did not correspond with a half-order reaction, as has been suggested by GULBRANSEN and ANDREW(2) for an oxide-contaminated surface. For part of this run the order of reaction was indeterminate, and thereafter reaction was apparently diffusion-controlled.

The metal samples for the two experiments were prepared by sub-division of a metal sheet, and the pieces produced were irregular in shape. However making the assumption that the surface area of each sample is proportional to its weight, the ratio of surface areas in the experiments is 1.6. This should be the same as the ratio of the reaction rate constants if rate of reaction is proportional to surface area as postulated. In fact, the ratio of k for the first addition of the two experiments was 2.2, reasonable agreement in view of the assumption made regarding surface area and weight of sample.

Experiments in which $P \simeq P_F$. Several experiments were then made at 550 °C with smaller 50 atomic per cent alloy samples, to examine the effect of composition on the rate of reaction. The results of a typical experiment are plotted in Fig. 3, as $\ln(P - P_F)$ against t, the value of P_f being obtained from the sample weight, hydrogen uptake and the curve of equilibrium pressure against composition at 550 °C(1).

Figure 3 consists of a series of straight lines in which the slope gradually decreases. [illegible] experiments confirm that the order of reaction is unity up to a hydride composition (ZrTi)$H_{0.45}$ within the pressure range 10–0.5 mm Hg. The values of k in min^{-1}

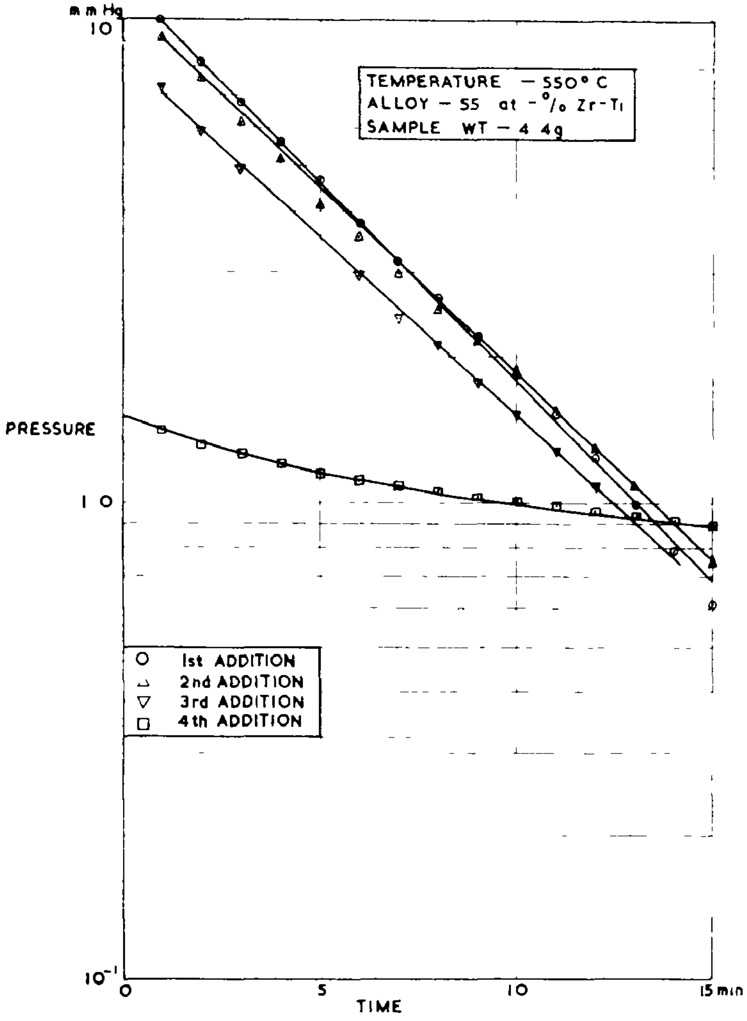


FIG. 2 Varying pressure experiment in which $P \sim P_f$

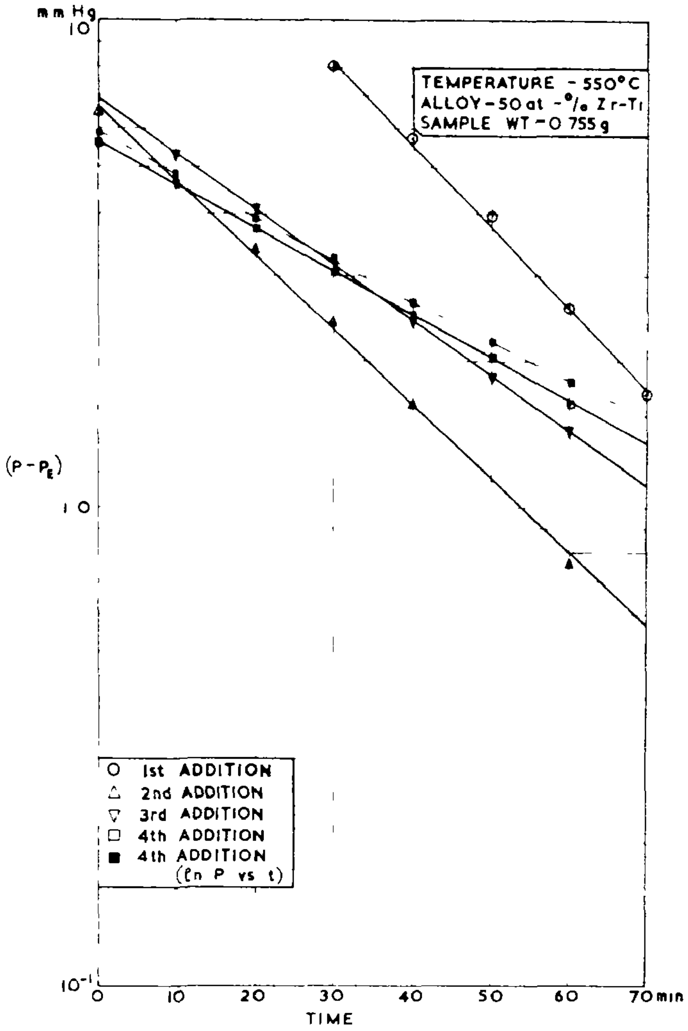


FIG. 3 Varying pressure experiment in which $P \sim P_f$

for the four additions were (in order) $3{\cdot}9 \times 10^{-2}$, $3{\cdot}6 \times 10^{-2}$, $2{\cdot}7 \times 10^{-2}$ and $2{\cdot}1 \times 10^{-2}$. The average area of the sample was estimated to be $3{\cdot}4$ cm^2 from its bulk dimensions. With the volume of the apparatus taken to be 1540 cm^3 and the temperature to be 293°K, the value of k was found for the first addition to be $2{\cdot}0 \times 10^{-6}$ g/cm^2 min mm Hg. Fig. 3 also shows that a curve would be obtained if $\ln P$ instead $\ln (P - P_e)$ were plotted against t.

Further runs confirmed unit order of reaction at hydrogen pressures down to $2{\cdot}0 \times 10^{-2}$ mm Hg, and gave values of the rate constant K in good agreement with those quoted above.

Experiments with materials machined in air and under oil. Alloy samples machined in air proved to be very unreactive, only some samples which had been abraded as described on p. 646 reacted with hydrogen. These again indicated that the reaction is first-order, and the rate constants were found to be $1{\cdot}55 \times 10^{-2}$ and $1{\cdot}42 \times 10^{-2}$ min^{-1}. The slower reaction rate (cf. $K = 3{\cdot}9 \times 10^{-2}$ min^{-1}) with almost identical sample area can be attributed to the formation of oxide in the production of the alloy strip. Abrasion of the strip evidently did not produce complete removal of the oxide layer.

The rate constant for an alloy sample machined under oil was found to be $4{\cdot}0 \times 10^{-1}$ min^{-1}. The sample was estimated to have an area of 12 cm^2 compared with $3{\cdot}3$ cm^2 for the sample machined in air. The ratio of the rate constants, $3{\cdot}7$, is further evidence of the deactivation produced by an oxide layer on the alloy surface.

Experiments at higher pressures. GULBRANSEN and ANDREW(3) found that, in certain pressure regions, the reaction between zirconium and hydrogen was diffusion-controlled and therefore zero-order with respect to pressure. Only with the fourth addition of the experiment shown in Fig. 2 was there any evidence of zero-order tendencies, and an experiment was performed at higher initial pressures of hydrogen to investigate this. A large sample of 55 atomic per cent alloy cut from a disk of material was used to minimize composition effects, and four successive additions of hydrogen were made. A fast rate of reaction was obtained and could not be observed with great accuracy. The results, plotted as $\ln P$ against t in Fig. 4, indicate that the order of reaction changes from unity at higher pressures, and that the pressure where the change occurs is lowered as the hydrogen content increases or the oxide layer thickens. Assuming that departure from first-order kinetics depends on hydrogen content, it is relevant that in the first addition the change occurs at 100 mm Hg and a composition $(ZrTi)H_{0{\cdot}2}$, and in the third addition at 25 mm Hg and $(ZrTi)H_{0{\cdot}9}$. No deductions can be made with confidence from the fourth addition. The average rate constant from the second and third additions was found to be $1{\cdot}4$ min^{-1}. When the sample was removed, the pieces of alloy were found to be badly cracked with macrocracks up to 30 μ wide, and some pieces had disintegrated into smaller fragments. This was presumably the result of high strains in the lattice produced by the rapid absorption of hydrogen.

The rate constant for the first addition of an experiment carried out at pressures below 10 mm Hg with similar material, was $4{\cdot}2 \times 10^{-1}$ min^{-1} for a sample of $7{\cdot}1$ g. This shows that the rate of reaction at the higher pressures is faster than expected, and the probable explanation is the increase in surface area produced by the cracking of the sample which was noted. This is also a possible explanation for the increase in slope between the first and subsequent additions illustrated in Fig. 4.

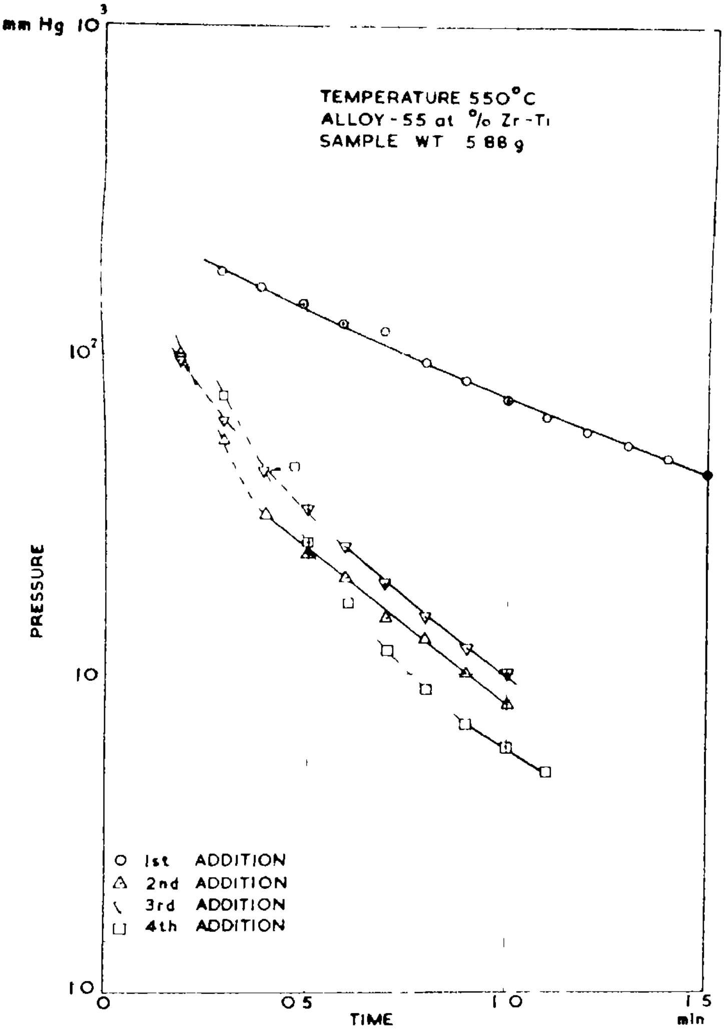


Fig 4 Varying pressure experiment with higher initial pressures

Reaction at constant pressure under static conditions

There was a lack of reproducibility in constant pressure experiments carried out at 550 C This was attributed to the pretreatment of samples before reaction samples were heated under vacuum to 850 C to remove oxygen or hydrogen absorbed in previous runs It is believed that varying amounts of oxide film reformed as the temperature was reduced from 850 to 550°C Reproducible results at 550°C in the varying-pressure runs were presumably obtained because (a) the experiment was of short duration and no additional significant amount of oxide film was formed, and (b) a single experiment gave sufficient data for the order of reaction and rate constant to be calculated

Reproducible results were obtained at 800°C they show the reaction rate decreasing with time, the effect being most pronounced with the run done at the lowest pressure (1 6 mm Hg) This decrease in reaction rate was attributed to the effect of the high value of equilibrium pressure of hydrogen above the alloy at 800°C To reduce this effect, the reaction temperature was lowered to 700°C and a series of experiments made at pressures ranging from 1·92 to 9·28 mm Hg Figure 5 shows a typical plot of uptake of hydrogen with time for a sample of alloy Runs made at identical pressures gave good reproducibility, showing that the effective surface area of the sample was not being altered by oxide film formation Theoretically the plot of hydrogen uptake with time should be a straight line In practice curves were obtained for the start of the runs indicating some deviation in the kinetic conditions However, for the major part of the runs straight lines were obtained From the slope of the lines in Fig 5 the rate of reaction was calculated A logarithmic plot of the reaction rate against hydrogen pressure was then constructed, and the best straight line drawn through the points (Fig 6)

Differences in the surface area of the samples used were taken into consideration when constructing Fig 6 by duplicating a run on the new sample, at the same pressure as that of a run on the previous sample In constructing the rate–pressure graph these two points were superimposed, thus giving a value for the ratio of the areas of the two samples This correction factor was used to express all results in terms of the area of the first sample which was taken as unity Equation (1) shows that, provided that there is a definine order of reaction, a plot of log dP/dt against log P will give a straight line of slope n, where n is the order of reaction The slope of this line gave a value of 1·0 It was therefore concluded that, for pressures between 1·92 and 9·28 mm Hg and a temperature of 700°C, the reaction between hydrogen and 55 atomic per cent zirconium–titanium alloy is first-order

Reaction under flow conditions with packed beds

Order of reaction In experiments with 50 atomic per cent alloy (series I and II), at constant temperature and for a given range of flow rates, first-order kinetics were obtained, a plot of ln $C_0/(C - C_E)$ against t was a straight line, of slope K where K is the rate constant for the reaction as previously defined Here C_0 is the inlet hydrogen concentration, C is the outlet hydrogen concentration, C_E is the equilibrium hydrogen concentration corresponding to the amount of hydrogen dissolved in the bed and t is the reaction time in seconds As has already been pointed out in the experimental section, the equilibrium concentration measured differs by a small amount from the true equilibrium concentration, but the fairly constant deviation in C_E and C does not significantly effect the kinetic plot

A typical plot is shown in Fig 7, from the slope of the graph K was found to be 1·07 sec^{-1} In experiments with 55 atomic per cent zirconium–titanium alloy that had been turned in air (series III), the kinetics of reaction were found to be half-order, not first-order In this case, a plot of ln $[C_0/(C - C_E)]^{1/2}$ against ln t, where the parameters are as above, was found to be a straight line of slope 45° These results were reproducible after removal of the hydrogen at 1050°C and pumping to an isolation pressure of 10^{-4} mm Hg

In experiments with the 55 atomic per cent alloy turned under oil (series IV), the bed was not activated before use, but merely heated to the reaction temperature of 450°C The results showed that the reaction was half-order as in series III, and had approximately the same rate constant

After the removal of the hydrogen by heating to 1050°C and pumping to an isolation pressure of 10^{-4} mm Hg, the reaction at 450°C was repeated This time,

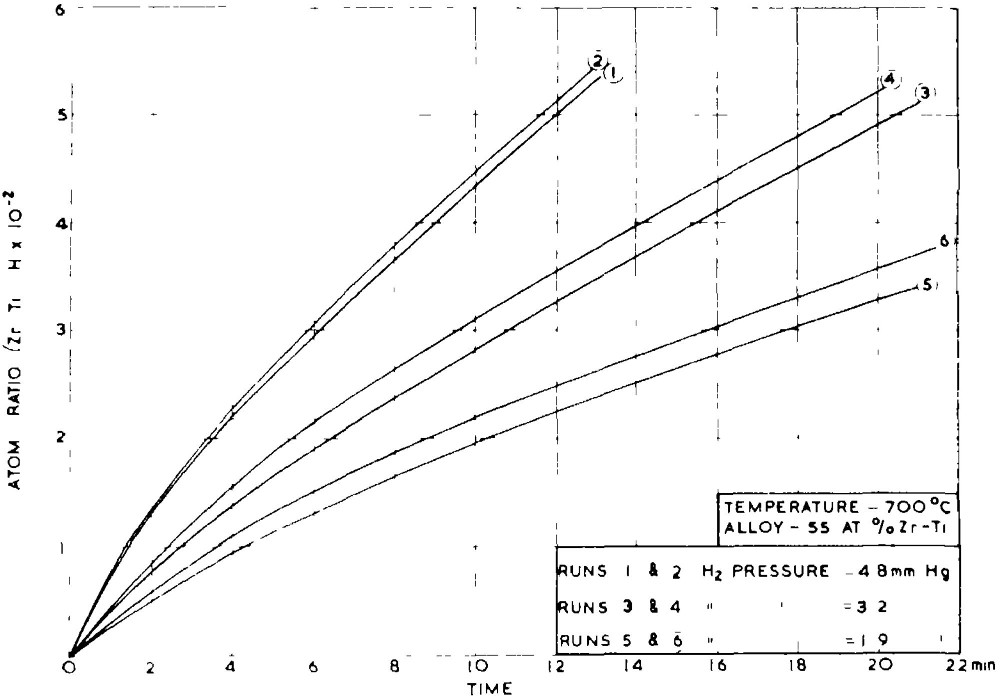


FIG 5 Constant pressure experiments rate of hydrogen uptake

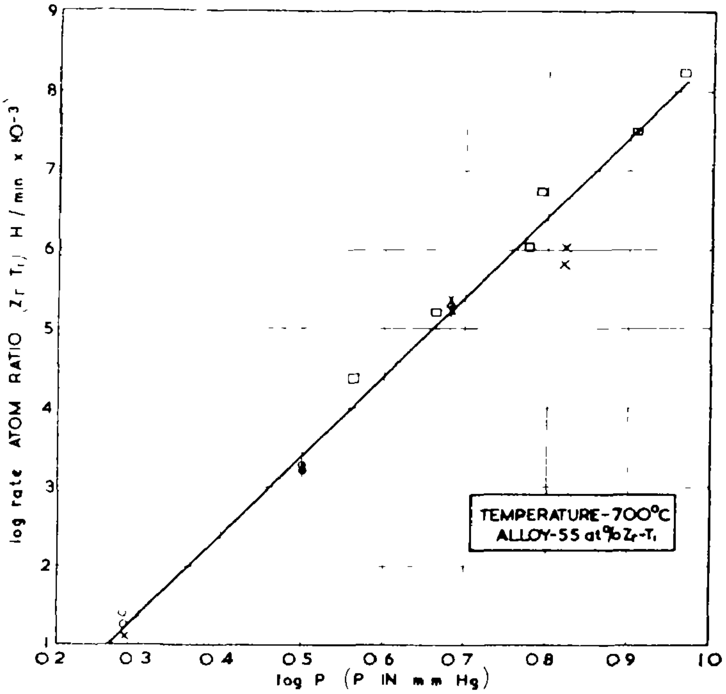


FIG 6 —Log plot of reaction rate against pressure in constant pressure experiments

however, the results did not fit the half-order plot, but showed first-order kinetics

These experiments lend further support to the belief that the order of reaction depends on the thickness of the protective oxide film on the surface of the metal If it is thin, the reaction is first-order, if it is thick, the reaction is half-order In the

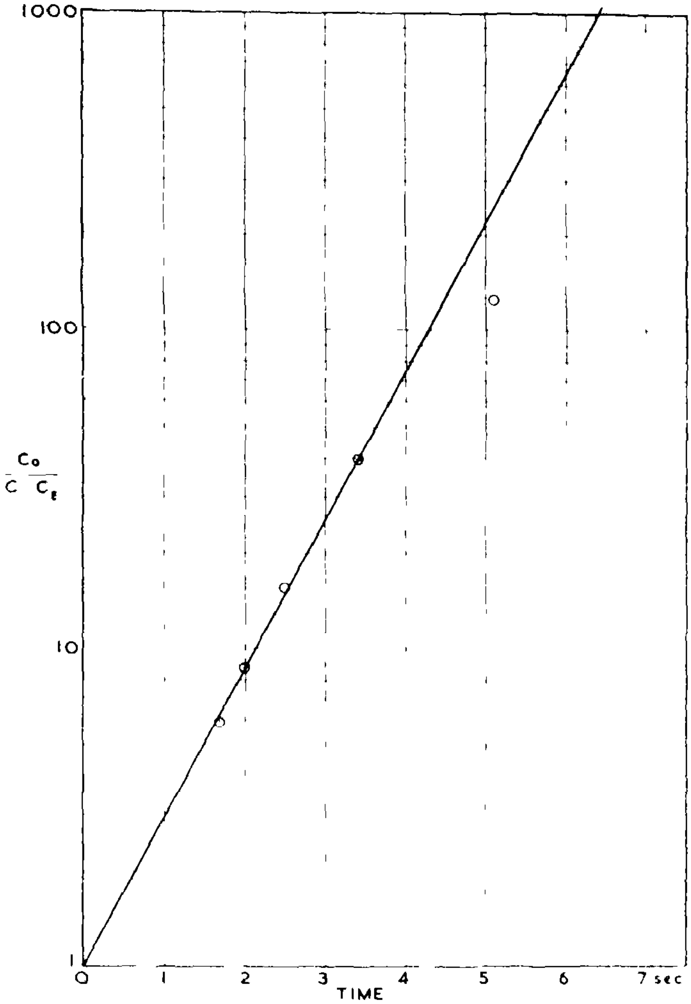


FIG. 7 Flow experiment first order rate plot at 570 C

intermediate range, when the oxide layer is not too thick, the reaction changes from half-order to first-order after heating to 1050°C and allowing some of the oxide ions on the surface to diffuse into the metal If the oxide layer is too thick, however, the amount which diffuses into the metal at 1050°C is insufficient to alter the order of reaction

Effect of temperature The results of experiments at different temperatures are given in Fig 8 as plots of ln K/T against $1/T$, where T is the absolute temperature, They show that the Arrhenius law was obeyed over the temperature ranges studied

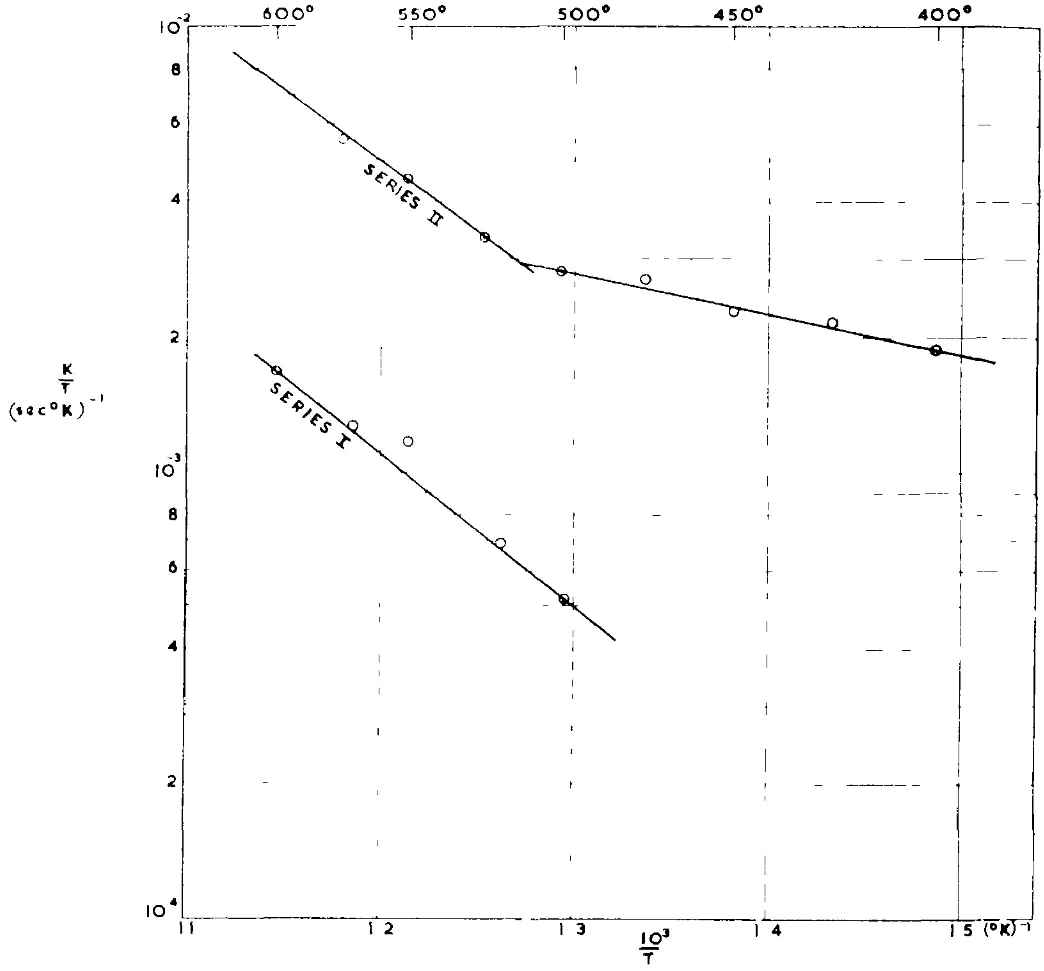


FIG 8 —Arrhenius plots for series I & II flow experiments

In the experiments of series I in the temperature range 500–600°C the rate constant varies with temperature according to the equation

$$\frac{K}{T} = 1\ 55 \times 10 \exp\left(-\frac{16,000}{RT}\right)$$

In series II, however, for temperatures between 520° and 570°C, the rate constant can be expressed by the equation

$$\frac{K}{T} = 5\ 20 \times 10 \exp\left(-\frac{15,400}{RT}\right)$$

whereas for temperatures below 520°C the equation is

$$\frac{K}{T} = 4\ 0 \times 10^{2} \exp\left(-\frac{4,100}{RT}\right)$$

The existence of two energies of activation for the reaction may possibly be caused by a difference in the rates of reaction of hydrogen with γ-Zr-Ti alloy and β-Zr-Ti alloy, which phases exist below and above 520°C The difference in the activation energies for the two processes shows that the reaction rate of hydrogen with the γ-alloy is much less temperature-sensitive than that with the β-alloy

Effect of packing density As the turnings used in series I and II experiments came from the same batch of material, the specific surface area should be approximately the same in both beds, thus one would expect the ratio of the reaction rates to be the same as the ratio of their packing densities, namely 3 9 From Fig 8 the ratio of the reaction rates at 550 C was found to be 4 5

Comparison of the rate constants of static and flow experiments

The results of both types of experiment can be expressed in the form of a rate constant $K = (kART/V)\,\mathrm{min}^{-1}$, which depends on the packing density A/V and the temperature T

Using suffixes S and F for comparable static and flow experiments at 550°C, respectively,

$$\begin{array}{lllll}
K_S \text{ (average)} & & & 3\,0 & 10^{-2}\,\mathrm{min}^{-1} \\
K_F & & & 2\,2 & 10^{-2}\,\mathrm{min}^{-1} \\
A_S & 3\,4\ \mathrm{cm}^2, & A_F & 3\,2 & 10^3\,\mathrm{cm}^2 \\
T_S & 293\ \mathrm{K}, & T_F & 823\ \mathrm{K} & \\
V_S & 1540\ \mathrm{cm}^3, & V_F & 148\ \mathrm{cm}^3 &
\end{array}$$

$$\frac{k_S}{k_F} \quad \frac{K_S V_S T_F A_F}{K_F V_F T_S A_S} \quad 3\,8$$

Thus the rate constant obtained from the static experiments is four times as great as that obtained from the dynamic experiments The agreement between the two types of experiment is reasonable, considering the large difference in packing densities It might be expected that the argon used in the dynamic experiments would exert a "blanketing" effect and reduce the rate of diffusion of hydrogen to the alloy surface

Reaction of hydrogen with zirconium under flow conditions

A small number of comparative experiments with zirconium metal were done under flow conditions After initial activation of the zirconium the results were reproducible

In the first experiment at 450 C, the reaction obeyed first-order kinetics, giving a value for the rate constant, K, of 1 54 sec^{-1} After re-activation at 1050°C and removal of the hydrogen, a repeat run at 450°C showed first-order kinetics, but the value of the rate constant had increased to 3 28 sec^{-1} After removal of hydrogen and further reactivation at 1050°C, repeat runs at 450°C confirmed the value of 3 28 sec^{-1} for K Runs were made at various temperatures in the range 400 470°C, the results plotted in the form log (K/T) against $1/T$ gave a straight line which can be represented by the equation

$$\frac{K}{T} = 9\,1 \quad 10^{3}\exp\left(\ \frac{17\,300}{RT}\right)$$

These experiments are the only ones known which show the reaction of zirconium and hydrogen to be first-order. Gulbransen and Andrew(3) showed the reaction to be diffusion-controlled but their study was at higher pressures, namely 1.0–5.0 cm Hg. It might be expected that a reaction which was first-order at low pressures (<0.7 mm Hg) would become diffusion-controlled at higher pressures. In the study of zirconium–titanium alloys, departures from first-order kinetics are only indicated at considerably higher pressures than those used in the study by Gulbransen and Andrew. There is thus some evidence that diffusion of hydrogen is more rapid in zirconium–titanium alloy than in zirconium.

From data obtained by Morton(5), the activation energy for the reaction of hydrogen with titanium was calculated to be 14.5 kcal/mole, and it is of interest that the value of the activation energy for the reaction of 50 atomic per cent zirconium–titanium alloy with hydrogen in the same temperature range, namely 15.7 kcal/mole, is intermediate between the values for zirconium and titanium.

Acknowledgement—This paper is published by permission of Mr. R. V. Moore, Managing Director of the Reactor Group of the United Kingdom Atomic Energy Authority.

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 657 to 660. Pergamon Press Ltd. Printed in Northern Ireland

ON THE VOLATILITY OF SOME POLONIUM COMPOUNDS

H. MABUCHI
Department of Chemistry, Faculty of Science, The University of Tokyo,
Bunkyo-Ku, Tokyo

(*Received* 10 *September* 1962, *in revised form* 12 *November* 1962)

Abstract—The volatility of thirteen polonium compounds which are extractable with organic solvents was investigated. The result of heating tests showed that all compounds resulting from the interaction of polonium with chelating agents volatilize below 200°C/1 atm.

DURING a study of the solvent extraction of trace amounts of polonium, KIMURA and the present author observed sublimation of the polonium extracts with dithizone at the unexpectedly low temperature of 120°C. Tests confirmed that the volatility of the polonium should be attributed to the dithizone compound itself and not to a thermal decomposition product.(1) Since this property has never been reported before and, in general, information on the volatility of inner complexes is rather lacking, a more extensive study has been made.

EXPERIMENTAL

Radioactive tracers

Copper tracer ^{64}Cu was produced by (d, p) reaction on copper with a cyclotron at the Institute of Physical and Chemical Research.

As silver and cadmium tracer, ^{110m}Ag and ^{115m}Cd obtained from Oak Ridge National Laboratory U.S.A. were used without further purification.

Radioactive tellurium was separated from fresh fission products and purified with cation and anion exchange resins.(2)

Polonium and radioactive lead and bismuth were prepared from active deposits in aged radon tubes. Radium-D-E-F mixtures were leached out from radon tubes, followed by the separation of one nuclide from another with an anion exchange resin.(3)

Preparation of samples for heating test

The organic layers containing the radioactive extracts were transferred onto stainless steel disks (2.5 cm in diameter). Then the organic solvents were vapourized at low temperature. The dried samples thus obtained were subjected to heating.

Heating

The disks were heated on a hot plate (Fig. 1) which was designed for the purpose of this experiment.

Activity measurement

The γ-activity of ^{210}Po was measured with a Lauritsen electroscope. The activities of ^{64}Cu, ^{110m}Ag, ^{115m}Cd, ^{129m}Te–^{129}Te and ^{210}Bi were measured with a end-window G-M counter. The soft-β-emitter ^{210}Pb was determined by measuring the β-rays from ^{210}Bi in radioactive equilibrium with the ^{210}Pb.

---

(1) K. KIMURA, H. MABUCHI, *Bull. Chem. Soc. Japan* **28**, 535 (1955).
(2) Y. SASAKI, *Japan Analyst* **4**, 637 (1955).
(3) T. ISHIMORI, *Bull. Chem. Soc. Japan* **28**, 432 (1955).

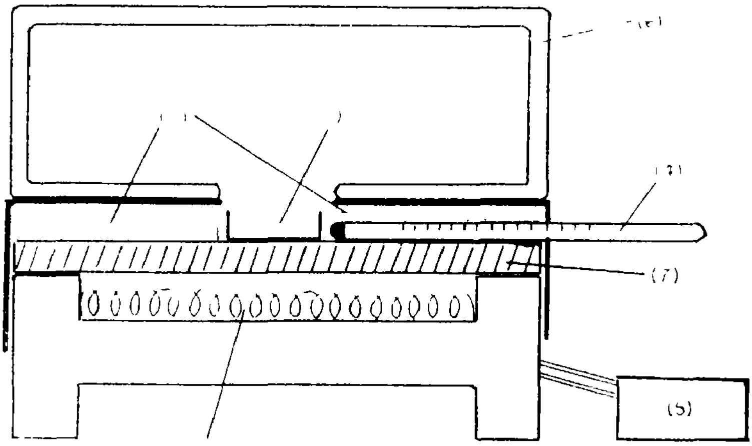


FIG. 1. Hot plate.
(1) sample disk
(2) felt
(3) electric heater
(4) thermometer
(5) variable transformer
(6) glass covering
(7) iron plate

RESULTS AND DISCUSSION

Heating tests on metal dithizonates

PARIAUD and ARCHINARD(4) observed the decomposition of the dithizonates of silver (186 C), lead (215 C), zinc (225 C), and copper (150 C) without appreciable sublimation when these compounds were heated from 150° to 250°C. In the present work radioactive isotopes were used so that only trace amounts of the complexes were concerned. The results obtained are summarized in Table 1. It is noticeable that tellurium, a lower homologue of polonium behaves just like polonium, whereas the others do not.

Heating tests on polonium compounds

Polonium often forms volatile compounds. The carbonyl, hydride and dimethyl compound are known to be highly volatile substances. CAIRO(5) found that the complex

TABLE 1. — VOLATILITY OF THE DITHIZONATES OF SEVERAL METALS

Element	Isotope used as tracer	Quantity used including carrier	Result (heating for 15 min)
Copper	^{64}Cu	180 μg	No sublimation
Silver	^{110m}Ag	1 μg	No sublimation
Cadmium	^{115m}Cd	1 μg	No sublimation
Tellurium	^{129m}Te, ^{129}Te	Tracer scale	120 C 14% sublimes 130 C 58% sublimes 150 C 65% sublimes
Lead	^{210}Pb	Tracer scale	No sublimation
Bismuth	^{210}Bi	Tracer scale	No sublimation

---

(4) J. C. PARIAUD, P. ARCHINARD, *Rec. Trav. Chim.* **71**, 634 (1952).

TABLE 2 — VOLATILITY OF VARIOUS POLONIUM COMPOUNDS[1]

No	Experimental conditions for the extraction of polonium			Activity retained after 15 min heating (%)			Lowest temp for sublimation (°C)
	Reagent	Solvent	Aqueous phase	100 C	150 C	200 C	
1	8-hydroxyquinoline	Chloroform	pH 2 in HNO_3	97	82	63	140
2	sodium diethyldithiocarbamate	Chloroform	pH 2 in HNO_3	99	79	43	110
3	thenoyltrifluoroacetone	Benzene	pH 8 in NH_4OH	98	70	70	—
4	thiourea	Chloroform	pH 8 in NH_4OH	104	69	41	120
5	sym -diphenylthiourea	Chloroform	pH 8 in NH_4OH	99	90	87	125
6	thiosemicarbazide	Chloroform	pH 8 in NH_4OH	101	81	29	120
7	1-phenylthiosemicarbazide	Chloroform	pH 8 in NH_4OH	103	78	48	130
8	diphenylcarbazone	Chloroform	pH 2 in HNO_3	91	33	15	95
9	diphenylcarbazide	Chloroform	pH 2 in HNO_3	77	19	10	90
10	diphenylthiocarbazone	Carbon tetrachloride	pH 2 in HNO_3	104	22	7	115
11	di-β-naphthylthiocarbazone	Carbon tetrachloride	pH 2 in HNO_3	99	91	44	150
12	KI, HCl	Isopropyl ether	0 5 M in KI 3 M in HCl	99	105	100	
13	KI, HCl	Methyl isobutyl ketone	0 5 M in KI 1 5 M in HCl	116	114	102	

chloride of polonium extracted by ketone volatilizes at a comparatively low temperature

In the present experiment, the volatility of polonium compounds which are extractable with organic solvents was studied The compounds investigated are tabulated in Table 2 together with the conditions for each extraction These compounds are divided into two groups according to their chemical nature

(a) compounds resulting from the interaction of polonium with chelating agents (1 ~ 11 in Table 2),

(b) compounds extracted into solvents in the absence of chelating agents (12 and 13 in Table 2)

The samples mounted on stainless steel disks were heated, and the polonium activity was measured in order to find the extent of sublimation The result is shown in Table 2 The 5th, 6th, and 7th columns of Table 2 show the percentages of polonium retained on the disks after 15 min-heating at 100°, 150°, and 200°C, respectively In the last column is listed the lowest temperature at which a noticeable decrease in polonium activity is observed This was determined by measuring the percentages of polonium retained on the disks after heating each compound for 30 min at various temperatures Thenoyltrifluoroacetone complex, ether extract and ketone extract were omitted from this test, because of difficulty in handling in the case of the TTA complex and of non-volatilization below 200 C in the case of the ether and ketone extracts

(1) All polonium compounds except Nos 12 and 13 sublime below 200°C/1 atm

(2) The volatility of the polonium compounds with chelating agents of similar type tends to decrease in the following order, though nothing decisive can be deduced because of the uncertainty of their chemical formulae

(a) thiourea sym-diphenylthiourea

(b) thiosemicarbazide 1-phenylthiosemicarbazide

(c) diphenylcarbazide ≿ diphenylcarbazone diphenylthiocarbazone di-β-naphthylthiocarbazone

(3) The volatility of the compounds with diphenylcarbazide, diphenylcarbazone, and diphenylthiocarbazone is noteworthy The first two sublime below 100°C/1 atm

From the results mentioned above, it follows that the low-temperature sublimation is not a peculiarity of polonium dithizonate, but is common to several complexes of polonium

The high volatility of these polonium compounds will find its application in separating polonium from other elements

Acknowledgements —The author wishes to express his sincere gratitude to Prof N SAITO and Dr Y YOKOYAMA of the University of Tokyo, and to Dr K KIMURA of Japan Atomic Energy Research Institute for their kind advices and most encouraging discussions

[5] A I CAIRO, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy Geneva* 1955, Vol 7 p 331 United Nations (1956)

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 661 to 665. Pergamon Press Ltd. Printed in Northern Ireland

STEAM DISTILLATION OF POLONIUM COMPOUND WITH DIPHENYLCARBAZIDE

H. MABUCHI
Department of Chemistry, Faculty of Science, The University of Tokyo,
Bunkyo-Ku, Tokyo

(*Received* 10 *September* 1962, *in revised form* 12 *November* 1962)

Abstract—Trace amounts of polonium can readily be steam distilled from 0.1 to 0.5 N nitric acid as the diphenylcarbazide complex. Chloride ion lowers the efficiency of the process. The separation is suitable for isolating Po from radium-D-E-F mixtures.

THERE are, in general, two kinds of vapourization techniques available for separating volatile substances from others: evaporation from solid surfaces and evaporation from solution. The distillation procedures hitherto used for separating polonium from elements such as lead or bismuth were in most cases based on the former technique, that is, sublimation of elemental polonium followed by the deposition on gold, platinum or nickel surfaces. Though this is a convenient and commonly used method in the analytical chemistry of polonium, there is one disadvantage, we can hardly expect complete vapourization. From this point of view, vapourization procedures using a liquid phase are desirable.

Previous work has shown that(1) the diphenylcarbazide complex deserves special attention, firstly because it forms a highly volatile compound with polonium which sublimes at as low a temperature as 90° C from solid surfaces, and secondly because it is fairly soluble in warm water. In view of these two properties of the reagent it seems very likely that we can distil polonium from aqueous solution, using diphenylcarbazide. The main purpose of this paper is to report the effects of the conditions on the separation of polonium by distillation of this complex.

EXPERIMENTAL

Preliminary experiment

Fifty millilitres of aqueous solution of polonium were taken in a Claisen-type distilling apparatus and 30 mg of diphenylcarbazide powder added. The solution was heated and distillation was carried on until 40 ml of solution were distilled off. The polonium was determined in the distillate. The larger part of the polonium appeared in the earlier portion of the distillate.

Polonium standard solution

Radium-F (^{210}Po) was separated from radium-D-E-F mixtures which were leached with concentrated nitric acid from aged radon tubes. For the separation of these mixtures, the anion exchange method by ISHIMORI(2) was applied. Radium-F thus obtained was divided into two parts, one of which was stocked as 3 M nitric acid solution and the other as 3 M hydrochloric acid solution.

Distillation procedure

The following procedure was adopted. Fifty millilitres of aqueous solution of polonium are transferred into a small all-glass distilling apparatus. After the addition of a definite amount of diphenylcarbazide powder into this solution, half the initial volume is distilled off The percentages of polonium distilled are calculated from measurements of the polonium activity in the remaining liquor

---

(1) H. MABUCHI, *J. Inorg. Nucl. Chem.* **25**, 657 (1963).

(2) T. ISHIMORI, *Bull. Chem. Soc. Japan* **28**, 432 (1955).

Determination of polonium

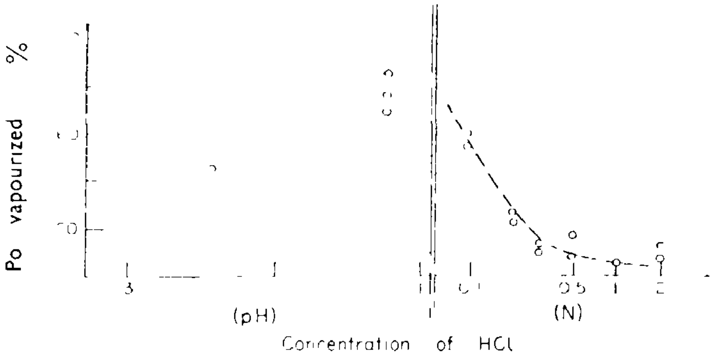
Radium-F contained in the aqueous solution was extracted with a carbon tetrachloride solution of dithizone at pH 1 The extract was removed onto a stainless steel disc and dried at about 30 C The α-activity of this sample was measured with a Lauritsen electroscope

RESULTS AND DISCUSSION

Effect of acidity on the efficiency of evaporation

Results for hydrochloric and nitric acid media are illustrated in Figs 1 and 2 In each case 30 mg of diphenylcarbazide was used

FIG. 1 Distillation of polonium from hydrochloric acid solution



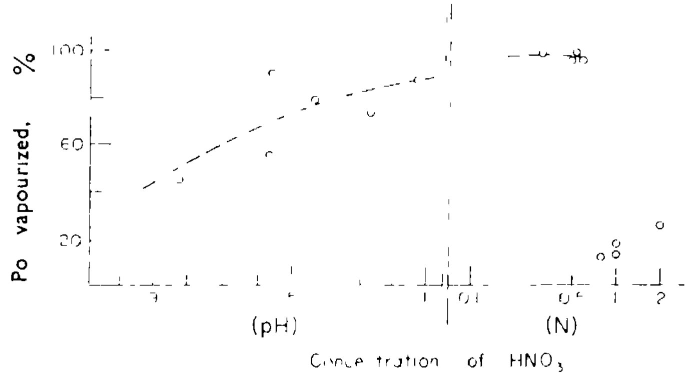


FIG. 2 Distillation of polonium from nitric acid solution

It may be noticed

(1) In general, the efficiencies are better for distillation from nitric acid solutions than from hydrochloric acid solutions

(2) In the case of nitric acid solution, almost complete evaporation of polonium may be expected between 0 1 and 0 5 N in nitric acid At an acidity of more than 0 5 N, decomposition of diphenylcarbazide takes place and a sudden decrease in efficiency is observed

(3) In the case of hydrochloric acid solution, the efficiency decreases gradually as the acidity increases and essentially no evaporation is observed above 1 N

Effect of the anion on the efficiency of evaporation

We have noticed above that the efficiency of evaporation of polonium from hydrochloric acid solution decreases as the acidity increases This seems to be due to the presence of chloride ion in the initial solution. This was confirmed by the following experiments.

The initial polonium solution in the distillation flask was adjusted to 0.3 N in nitric acid and a given concentration in sodium chloride. As before, the amount of diphenylcarbazide used was 30 mg. In this way the concentration of sodium chloride was varied up to 1 N. The percentage of polonium vapourized at each chloride concentration is shown in Fig. 3. For comparison, the effects of the presence of sodium nitrate and sodium sulphate were investigated in the same way. The results are illustrated in Figs. 4 and 5, respectively. The result clearly shows the interference of chloride ion with the vapourization of the polonium compound. This effect is, presumably, due to the strong complexing of polonium by chloride ion which would prevent the element from forming diphenylcarbazide compound.

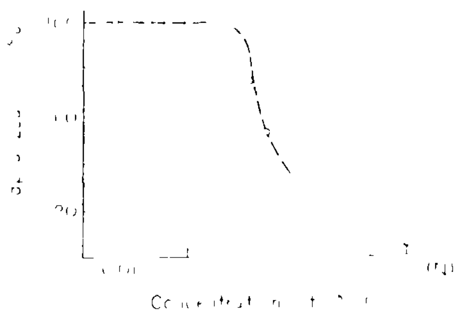


FIG. 3 —Effect of Cl^-

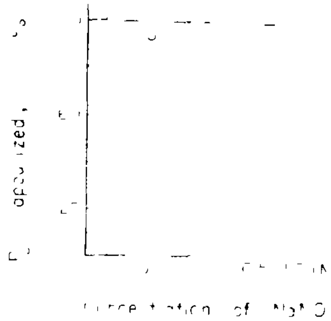


FIG. 4 Effect of NO_3^-

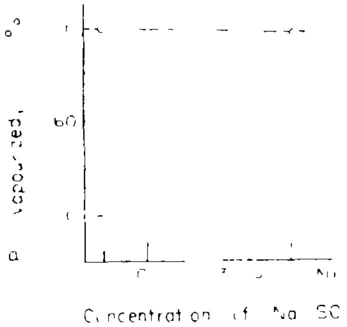


FIG. 5 Effect of SO_4^{2-}

Effect of varying the concentration of diphenylcarbazide

In Table 1 is shown the result of the vapourization experiment, where the amount of diphenylcarbazide used was varied. The acidity was kept constant (0.3 N in nitric acid) in all these runs. The effect of diphenylcarbazide is clearly shown in Table 1 and we notice that diphenylcarbazide concentration of 0.83×10^{-4} M/L (1 mg/50 ml) is sufficient to distil off polonium under these conditions.

TABLE 1 EFFECT OF DIPHENYLCARBAZIDE CONCENTRATION ON THE EFFICIENCY OF VAPOURIZATION

Diphenylcarbazide added (mg/50 ml)	Po vapourized (%)
20	99
5	99
5	100
1	98
1	99
0.8	10
0.8	5
0.5	8
0.5	22
0.3	4
0.3	14
0	0

Treatment of the distillate

To use this separation procedure it is necessary to know how to treat the distillate, for the polonium contained in it may possibly be volatile and so may be dissipated by careless treatment The following treatments were studied

(a) Evaporation of the distillate One millilitre of the distillate (polonium activity 1.9 div min^{-1} ml^{-1}) was transferred onto a glass disk and then dried on a water bath The activity of polonium retained on the disk was measured with a Lauritsen electroscope Such procedure was carried out three times The results are tabulated in Table 2, together with the values obtained when, for comparison, 0.1 ml of 30 per cent hydrogen peroxide or concentrated nitric acid was added into the sample

TABLE 2 DECREASE OF POLONIUM ACTIVITY ON DRYING UP THE DISTILLATE

Polonium activity retained in the dish after drying up (div/min)		
No reagent added	H_2O_2 added	HNO_3 added
1.02	1.96	1.84
1.44	1.86	1.85
1.68	1.85	1.87

(b) Extraction with carbon tetrachloride—One millilitre of the distillate was extracted with an equal volume of carbon tetrachloride in a separatory funnel for 3 min The organic layer was transferred to a stainless steel disc, dried at room temperature and the activity measured The results are shown in Table 3

It is clear from these two experiments that the polonium in the distillate is volatile and extractable with carbon tetrachloride Presumably the polonium exists in the distillate in the form of the diphenylcarbazide compound If such assumption is correct, oxidizing agents such as hydrogen peroxide or nitric acid must prevent vapourization of polonium by decomposing the complex This is proved by the data

TABLE 3. EXTRACTION OF POLONIUM FROM THE DISTILLATE WITH CARBON TETRACHLORIDE

Polonium activity extracted (div./min)	(%)
1.40	74
1.67	88
1.31	69

in the 2nd and 3rd columns of Table 2. Therefore, it is essential to add oxidizing agents before further treatment of the distillate.

Application of the method to separation of radium-F from radium-D-E-F mixtures

The steam distillation of polonium described above was applied to the carrier-free separation of radium-F from its parent nuclides, radium-D and radium-E. The procedure used is as follows.

Fifty millilitres of nitric acid solution of radium-D-E-F mixtures are taken in an all-glass distilling apparatus. The acidity of the solution is adjusted to 0.3 N in nitric acid. After the addition of 30 mg of diphenylcarbazide, the distillation is carried out until half the solution is distilled off.

TABLE 4.—DISTRIBUTION OF RADIUM-D, -E, -F IN EACH FRACTION AFTER DISTILLATION (%)

	Distillate	Remaining liquor	Washing solution
Radium-D		97	0.1
Radium-E		100	0.2
Radium-F	56	7	37

An example of separation by this procedure is seen in Table 4. The percentages in the table show the distribution of each nuclide in the distillate, the remaining liquor, and the nitric acid solution used for washing the inside of the condenser. The determination of three nuclides was done by the use of their decay characteristics: radium-E by its pure β-activity and radium-D by the growth of its daughter nuclide radium-F.

As shown in Table 4, separation is nearly complete and radiochemically pure radium-F is found in the distillate. This aqueous distillate does not contain noticeable amounts of organic reagent.

Acknowledgement—The author wishes to thank Prof. N. SAITO, Dr. Y. YOKOYAMA and Dr. K. ISHIMURA for their invaluable advices and discussions.

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 667 to 675. Pergamon Press Ltd. Printed in Northern Ireland

OXYGEN EXCHANGE BETWEEN CO AND CO_2

C. A. BANK[1] and E. A. TH. VERDURMEN
F.O.M. – Laboratorium voor Massascheiding, Kruislaan 407, Amsterdam O

(*Received* 20 *September* 1962, *in revised form* 20 *November* 1962)

Abstract—The exchange of oxygen between CO and CO_2 has been studied with ^{18}O as a tracer, ov a temperature range from 800–900°C, in a transparent quartz vessel. No exchange of oxygen betwee the gases and the quartz has been observed, except at 900°C in a packed vessel. The CO/CO_2 exchang appears to be at least partly heterogeneous. Rather small amounts of water enhance the exchang rate. The exchange rate depends on the CO_2 pressure to the first power. At 820 and 850°C the ra is independent of CO pressure. A mechanism is discussed. At 900°C the CO/CO_2 exchange probab occurs partly in the gas phase. A comparison is made between the results on CO/CO_2 isotop exchange studied with carbon isotopes as the tracer, and our results.

ISOTOPIC exchange, around 900°C, in CO–CO_2 mixtures was studied by BRANDNE and UREY[2], using ^{13}C as a tracer. The reaction in a quartz vessel was found to b heterogeneous, and the rate of exchange was independent of the total pressure an composition of the gas mixture. NORRIS and RUBEN[3] studied the isotopic exchang with ^{14}C as a tracer. The reaction followed the rate law: rate $= k(p_{CO})^{0.73}(p_{CO_2})^{0.8}$. A probable mechanism appeared to be bimolecular exchange between the reactan adsorbed on the surface. The data of these workers, like those of BRANDNER an UREY, were quite poorly reproducible. HAYAKAWA[4] using ^{13}C as a tracer, obtaine a rate law

$$\text{rate} = k\, p_{CO_2} \frac{p_{CO}}{1 + b\, p_{CO}}$$

The rate determining process seems to be a bimolecular exchange reaction betwee the two reactant species adsorbed on quartz.

The isotopic exchange between CO and CO_2 has been studied here with ^{18}O as tracer in the temperature range 800–900°C. Previously, it is not obvious that one studying the same exchange reaction, using an oxygen or a carbon isotope as a trace

EXPERIMENTAL

Gases

Natural carbon dioxide was taken from a gas cylinder: purity 99.5 per cent carbon dioxid Natural CO was prepared by reduction of carbon dioxide with Zn at 400°C. The natural gases we enriched by thermal diffusion.

All gases were purified by keeping the gases for some hours at liquid air temperature; the gas were pumped and stored. Mass spectrometric analysis showed satisfactory purity.

---

[1] C. A. BANK, Thesis, University of Amsterdam (1962).

[2] J. D. BRANDNER and H. C. UREY, *J. Chem. Phys.* **13**, 151 (1945).

[3] T. H. NORRIS and S. RUBEN, *J. Chem. Phys.* **18**, 1595 (1950).

[4] T. HAYAKAWA *Bull. Chem. Soc. Japan* **26**, 165 (1953).

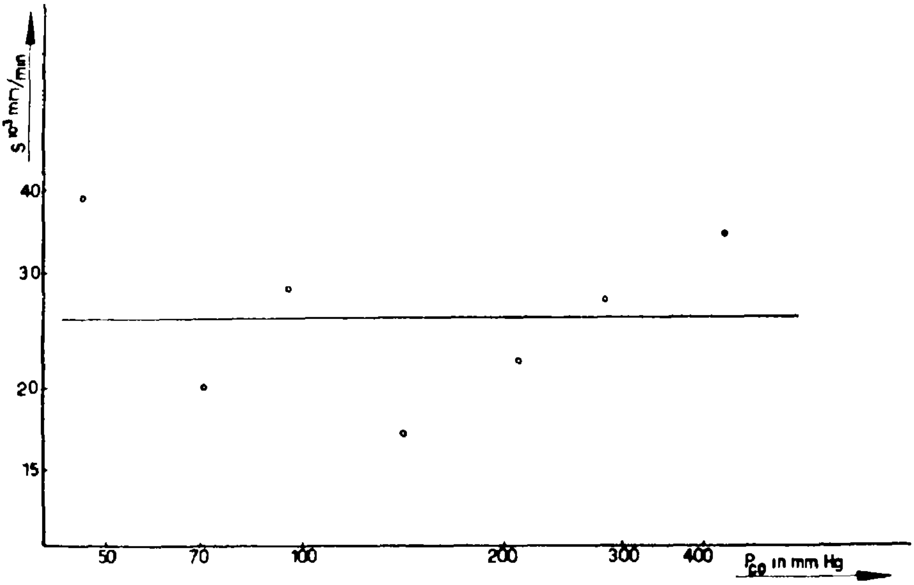


FIG. 1 – Dependence of rate on CO pressure at 820°C.
Calculated slope 0.00 ± 0.17

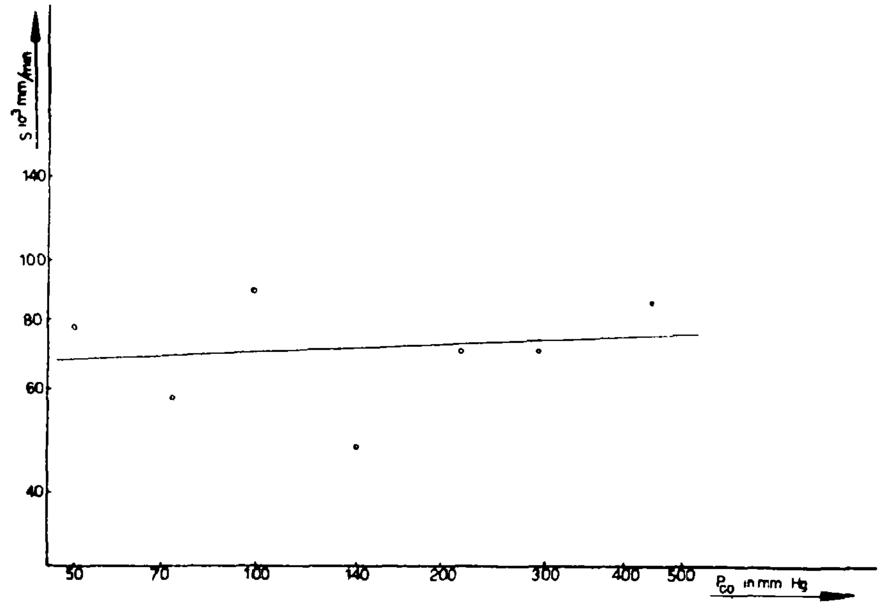


FIG. 2. Dependence of rate on CO pressure at 850°C.
Calculated slope 0.04 ± 0.12

Apparatus

The reactions were performed in a 30 mm dia. cylindrical transparent quartz vessel, length about 13 cm and volume 89 ml. The vessel was placed in a resistance-heated furnace. The furnace temperature was maintained constant to ± 5°C. The temperature gradient along the reaction vessel was less than 10°C. The required vacuum (about 10^{-5} mm mercury) was obtained by a rotary oil and a mercury diffusion pump. The volume of the vessel which was not at the reaction temperature was less than 1 per cent.

Procedure

The reaction vessel was first evacuated for several hours at the reaction temperature. The gases were mixed and subsequently led into the quartz vessel. The inlet pressure of the gas mixture was read on a mercury manometer. After reaction the carbon dioxide from the samples was frozen out in liquid air. The components of the samples were analysed separately by a conventional mass spectrometer.

RESULTS

The rate of exchange S, is defined by⁽⁵⁾

$$S = -\frac{1}{t}\frac{p_{CO}p_{CO_2}}{p_{CO}+p_{CO_2}}\ln(1-F) \qquad (1)$$

p_{CO} and p_{CO_2} signify the pressures of CO and CO_2 in the reaction mixture. t is the exchange time and F is the relative exchange, or exchange fraction

$$F = \frac{x_t - x_0}{x_\infty - x_0},$$

wherein x_t is the fractional content of ^{18}O in CO or CO_2 at time t, and x_∞ and x_0 are the values for this fraction at $t = \infty$ and $t = 0$. The values of x_∞ have been calculated from the fractional ^{18}O content at $t = 0$ and the mixing ratio of the gas components. In this calculation we assumed at $t = \infty$ a proportional distribution of ^{18}O between the gas components. A possible isotope effect was neglected.⁽⁶⁾

The dependence of the exchange rate S upon the reactant concentrations is given in the general form

$$S = kp_{CO}{}^{n}\, p_{CO_2}{}^{m} \qquad (2)$$

A log–log plot of S as a function of the pressure of CO, at constant CO_2 pressure, should give a straight line with slope n. A similar plot of S as a function of the pressure of CO_2, at constant CO pressure, should give a straight line with slope m. The results are reported in the Figs. 1–6. The precision of all ^{18}O contents is between 1 and 2 per cent. In all these experiments no measurable amount of ^{18}O exchanged with the surface oxygen.

The values of the exponents m and n, obtained from the plots, are summarized in Table 1. Calculations have been made by applying the method of least squares.

TABLE 1. VALUES OF EXPONENTS n AND m

Temp. (°C)	n	m
820	0.00 ± 0.17	1.41 ± 0.15
850	0.04 ± 0.12	0.99 ± 0.05
900	0.67 ± 0.05	1.01 ± 0.03

---

(5) H. McKay, *Nature, Lond.* **142**, 997 (1938); *J. Amer. Chem. Soc.* **65**, 702 (1943).

(6) H. C. Urey, *J. Chem. Soc.* 562 (1947).

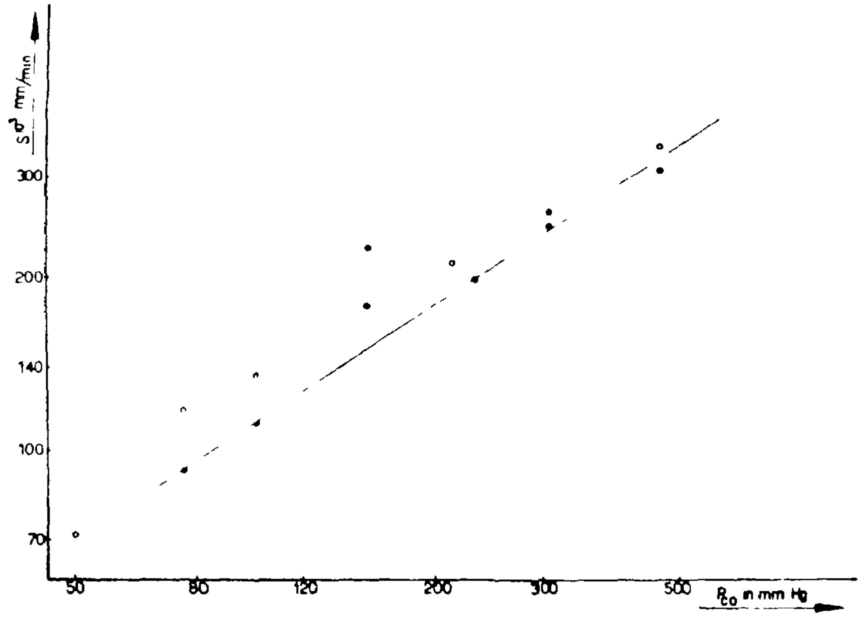


Fig 3 Dependence of rate on CO pressure at 900°C
Calculated slope 0 67 ± 0 05
From a comparison of the experiments expressed by black points and open circles the reproducibility of the rate measurements can be seen

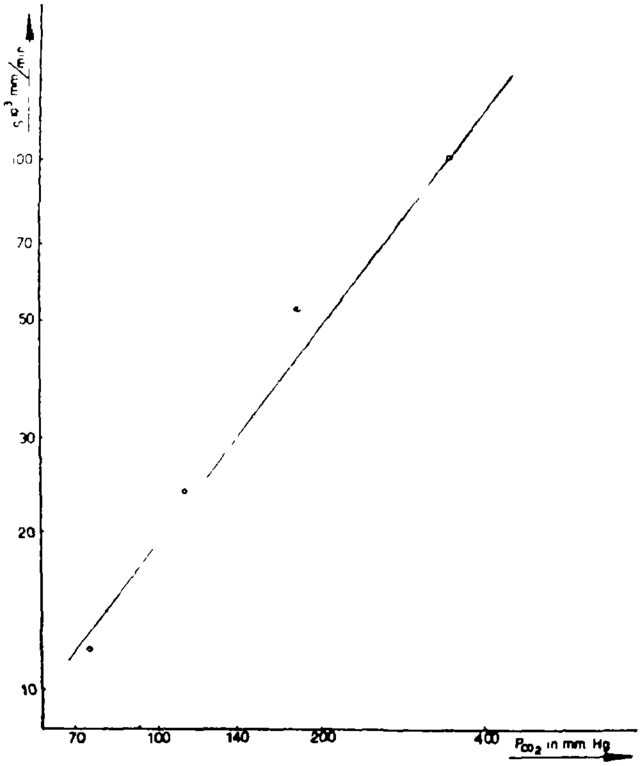


Fig 4 —Dependence of rate on CO_2 pressure at 820°C
Calculated slope 1 41 + 0 15

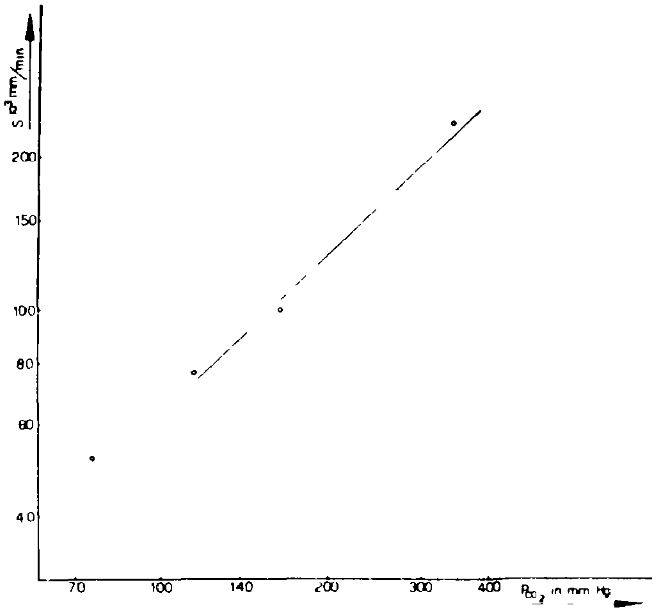


FIG. 5 – Dependence of rate on CO_2 pressure at 850°C
Calculated slope 0.99 ± 0.05

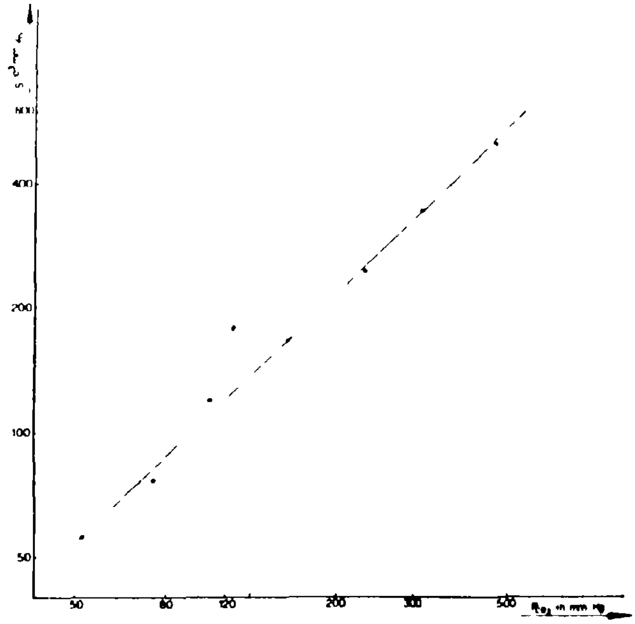


FIG. 6 Dependence of rate on CO_2 pressure at 900°C
Calculated slope 1.01 ± 0.03

Figure 7 is a typical plot of log $(1 - F)$ as a function of t. (Each point was obtained by performing a new experiment.) According to equation (1), the plot should be a straight line for a particular mixture. The actual plot shows a higher initial rate. Experiments showed an influence of the pretreatment of the reaction on this initial rate. We did not study this phenomenon further, but possibly it is due to a rapid chemisorption process. Direct connection of the reaction vessel to the ionization chamber of a mass spectrometer would make it possible to follow the exchange as a function of time and to verify this higher initial rate more accurately.

After each experiment the ^{18}O contents of the CO and of the CO_2 were determined by mass spectrometric analysis. The exchange fraction F was calculated from the values of x_t, x_0 and x_∞. By substitution of this fraction F in expression (1) the rate of exchange S was obtained. The exchange time was chosen in such a way that an exchange fraction was obtained with $0.10 < F < 0.40$.

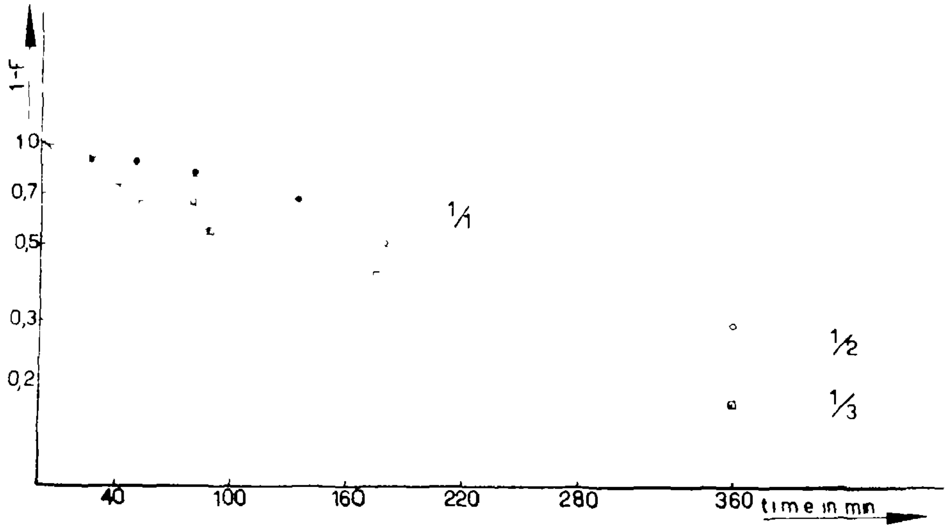


FIG. 7. Semilogarithmic plot of $1 - F$ vs. time at 900° C.
Mixing ratio CO/CO_2 1/3. Total pressure 200 mm Hg.
Mixing ratio CO/CO_2 1/2. Total pressure 450 mm Hg.
Mixing ratio CO/CO_2 1/1. Total pressure 300 mm Hg.

To test for heterogeneity the vessel was packed with crushed quartz, increasing the surface to volume ratio with a factor 38. Some results are given in Table 2. The values

TABLE 2. INFLUENCE OF PACKING ON THE RATE OF EXCHANGE
(Surface to volume ratio increased thirty-eight fold)

Temp (° C)	p_{CO} (mm)	p_{CO_2} (mm)	Ratio of rates in packed and unpacked vessels
820	73	218	2.6
820	225	337	1.7
850	75	227	3.5
850	163	225	2.6
900	75	227	2.1
900	226	226	2.4

of $[\log(1 - F)]/t$ have been compared for the packed and unpacked vessel. The exchange rate is enhanced two to three times. In the packed vessel at 900°C a slow exchange has been found between the surface oxygen and the oxygen of CO and CO_2. In one experiment CO_2 of ^{18}O content 0.75 per cent, pressure 400 mm mercury, lost about 14 per cent of its excess ^{18}O in 90 min. CO, with ^{18}O content 0.69 per cent, pressure 400 mm mercury, lost about 11 per cent of its excess ^{18}O in 90 min. At 850 and 820°C in the packed vessel no measurable exchange with the surface oxygen has been found. The numbers in Table 2 have been corrected for this loss of ^{18}O to the surface.

Possibly traces of water are still present as an impurity in the gases. Therefore, the influence of water-vapour has been studied. In Table 3 the effect of different amounts of water, at 900°C, is given. The exchange rate increases by addition of water. Only in experiment 3.5 some ^{18}O (4 per cent) has been lost, possibly due to the large amount of water.

TABLE 3. INFLUENCE OF WATER VAPOUR ON THE RATE OF EXCHANGE
Temperature 900°C. Mixing ratio CO/CO_2 equal to 1:1. Total pressure 302 mm Hg
^{18}O-content at $t = 0$: CO 0.664%, CO_2 0.200%

		P_{H_2O} mm Hg	Time min	^{18}O-content (%) CO	CO_2	F_{CO}	$-\log(1 - F_{CO})$
3.1	Dry	0.0	202	0.519	0.262	0.47	
3.2	Dry	0.0	100	0.587	0.230	0.25	0.13
3.3	Wet	0.4	100	0.560	0.251	0.35	0.19
3.4	Wet	3.4	100	0.480	0.285	0.60	0.40
3.5	Wet	18.0	100	0.389	0.318	0.90	1.00

From the data k values have been calculated. At 820 and 850°C we used the rate law $S = kp_{CO}^{n}\,p_{CO_2}^{m}$ with n equal to zero and $m = 1$, but at 900°C we calculated k from this rate law with $n = -0.67$ and $m = 1$. The k values are given in Table 4.

TABLE 4. RATE CONSTANTS (k) BETWEEN 800 AND 900°C

Temp (°C)	$k \quad 10^4$	
820	2.0	0.2
850	5.5	0.3
900	0.38	0.01

In none of our experiments has carbon deposition been observed. In several experiments we verified the mixing ratio CO/CO_2 after exchange. No difference with the initial ratio was found. Thus, there is no evidence for occurrence of the Boudouard equilibrium $2CO \rightleftharpoons C + CO_2$. At 900°C this equilibrium is more than 97 per cent displaced towards the side of CO (7).

(A. BANK, E. A. TH. VERDURMEN, A. E. DE VRIES and F. L. MONTERIE, *J. Inorg. Nucl. Chem.* **17**, 298 (1961).

DISCUSSION

Though the increase in exchange rate is much smaller than the change in surface to volume ratio, the data reported in Table 2, comparing experiments in a packed and an unpacked vessel suggest the reaction to be at least partly heterogeneous. The data of Table 3 show that rather small amounts of water can influence the exchange rate to a considerable extent. As a consequence of the heterogeneity and the possible presence of different trace amounts of water the exchange reaction cannot be expected to be quite reproducible.

So, we conclude from the data in Table 1 that in the temperature range 800–900°C the exchange rate depends on the CO_2 pressure to the first power ($m = 1$). At 820°C and 850°C the rate is independent of CO pressure ($n = 0$). At 900°C the exchange rate depends on CO pressure, with $n = 1$.

The measurements can be interpreted by the following mechanism. At the temperature involved CO is adsorbed (probably chemisorbed) to the maximum amount possible at that temperature. Exchange occurs by collision with CO_2 molecules from the gas phase. The rate dependence on CO pressure at 900°C can be ascribed to the appearance of a homogeneous CO/CO_2 reaction at higher temperatures.

Next, a mechanism involving the oxygen of the surface must be considered. In the unpacked vessel, no exchange between the oxygen of the gases and the surface oxygen has been measured even at 900°C. In the packed vessel, however, exchange with the surface oxygen has been observed at 900°C. It is assumed that this oxygen exchange occurs in two steps: exchange between the oxygen of the gas and the oxygen of the surface layer of the quartz, and next diffusion of the oxygen into the lattice. For both processes an activation energy can be defined.

The geometric area of the reaction vessel is 130 cm^2. If we assume the surface layer to be a layer of oxygen atoms, the number of those atoms is of the order of 10^{17}. The total number of particles in the gas phase, at a pressure of 400 mm mercury, is of the order of 10^{21}. As the accuracy of the mass spectrometric analysis was about 1 per cent, exchange between the gas and the surface layer could not be measured. In the packed vessel the surface area of the quartz has been determined by the B.E.T. method. The area was found to be 3600 cm^2. Hence, the number of O-atoms at the surface is of the order of 10^{19}. As mentioned above, in experiments with CO and with CO_2 in a packed vessel, the gas lost 10 per cent of its excess ^{18}O. The number of O-atoms of the surface, involved in this exchange must be of the order of 10^{20}. This is the number in about ten layers. So, it seems justified to consider the observed rate of oxygen exchange between the gases and the packing as a measure of the rate of oxygen diffusion into the lattice. We have no data about the rate of oxygen exchange between the gases and the surface layer of the quartz. If this oxygen exchange between CO and the surface layer is a rapid process, a mechanism that could account for the CO/CO_2 exchange data is as follows. Rapid oxygen exchange between the CO and the surface layer is followed by a slower, rate-determining, exchange of oxygen between the surface layer and the CO_2 from the gas phase.

If this mechanism is the right one a comparison with the measurements of BRANDNER and UREY,(2) NORRIS and RUBEN(3) and HAYAKAWA cannot be made, as they were using carbon isotopes as the tracer and in this mechanism no carbon exchange between CO and CO_2 occurs.

The values of k at 820°C and 850°C, reported in Table 4, are of the same magnitude the k values at 799°C and 850°C, reported by NORRIS and RUBEN This agreement in magnitude suggests we studied the same process by using each a different isotope

Otherwise our results do not fully agree with those of the other workers NORRIS and RUBEN determined the exponents, in the rate law $S = kp_{CO}^{n}p_{CO_2}^{m}$, from measurements at 850°C They assumed the values of n and m to apply over the temperature range 800–900°C This assumption is not valid over the temperature range involved, according to measurements At 900°C we found that the rate was dependent on CO pressure, at 850 and 820°C we did not

HAYAKAWA's rate expression has the form of a product of adsorption isotherms. The rate determining process seems to be a bimolecular exchange reaction between the two reactant species adsorbed on quartz. It is necessary to assume the adsorption of CO on the active surfaces is moderate, but CO_2 is rather weakly adsorbed, since in the experimental rate law

$$R = k\ p_{CO_2}\ \frac{p_{CO}}{1 + b\ p_{CO}},$$

only the CO factor has the form of a Langmuir adsorption isotherm Thus, as in our experiment, the rate is found to be proportional to CO_2 pressure Our conclusion that exchange possibly occurs between CO adsorbed at the quartz surface and CO_2 from the gas phase, is given by HAYAKAWA as an alternative mechanism

The dependence of exchange rate on CO pressure found by HAYAKAWA is different from our results This should not necessarily lead to different interpretations, except at 900°C where we assume the appearance of a homogeneous exchange reaction

From our measurements we could not exclude an exchange mechanism via the surface oxygen in the way we described above The rates measured by HAYAKAWA in the same temperature range correspond with our measurements This may be evidence that we studied the same reaction by using a different tracer In both experiments the influence of water is the same, though we measured a larger enhancement of the exchange rate by addition of water

Acknowledgements –We are indebted to Professor Dr J A A KETELAAR for discussions and helpful suggestions We also thank Professor Dr J KISTEMAKER and Dr A E DE VRIES for their stimulating interest Mr F L MONTERIF kindly performed the mass analyses

This work is part of the research programme of the Stichting voor Fundamenteel Onderzoek der Materie (Foundation for Fundamental Research on Matter) and has been made possible by financial support from the Foundation Z W O (Netherlands Organisation for Pure Scientific Research)

J Inorg Nucl Chem , 1963, Vol 25, pp 677 to 682 Pergamon Press Ltd Printed in Northern Ireland

THE EXCHANGE OF OXYGEN BETWEEN CO$_2$ AND O$_2$

C A Bank and E A Th Verdurmen
FOM—Laboratorium voor Massascheiding, Kruislaan 407, Amsterdam, O

(*Received* 20 *September* 1962, *in revised form* 20 *November* 1962)

Abstract The exchange of oxygen between CO$_2$ and O$_2$ has been studied with ^{18}O as a tracer in a transparent quartz vessel over a temperature range between 800 and 900 C No exchange of oxygen between the gases and the quartz has been observed, except in a packed vessel at 850 and 900 C Based on experiments at 850 and 900°C, a rate law is derived The behaviour between these temperatures is in reasonable agreement with the results obtained by studying the influence of packing the reaction vessel Mechanisms are discussed

Up to the present results have been published on the exchange of ^{18}O in the system CO$_2$ O$_2$ only on Pt-asbestos and CuO$^{(1\ 2)}$ For these materials a measurable exchange occurs at 600°C In 1958 some preliminary results are reported by Bank$^{(3)}$ Then the exponents *m* and *n* in the empirical rate law $S = kp_{CO_2}{}^{m}\ p_{O_2}{}^{n}$ were calculated, in the following manner

The rate of exchange *S* was determined for three independent mixing ratios Values for *k*, *m* and *n* were obtained by solving three equations However, it has appeared that the values of *S* must be very accurate before this method can be applied The more recent results are not in accord with those obtained in the past In this paper an empirical rate law is derived in the way that has been described in our preceding paper about oxygen exchange between CO and CO$_2$

EXPERIMENTAL

Natural oxygen gas of purity 99 5 per cent oxygen was taken from a gas cylinder Enriched oxygen was obtained by thermal diffusion of the natural gas Oxygen enriched in this way contained an appreciable amount of argon The argon was separated from the oxygen by passing the gas mixture through a column of molecular sieves (Linde type 4 A) modified by the addition of small amounts of water at liquid air temperature The oxygen was sorbed and the argon remained in the gas phase Excellent separation could be effected$^{(4)}$

Gases were purified by keeping the gases for some hours at liquid air temperature, the gases were pumped and stored Mass spectrometric analysis showed satisfactory purity In our previous paper, the preparation of CO$_2$ is already described A description of the apparatus and of the experimental procedure appears in the same paper

RESULTS

The rate of exchange *S* is defined by$^{(5)}$

$$S = -\frac{1}{t}\frac{p_{CO_2}\ p_{O_2}}{p_{CO_2}+p_{O_2}}\ln(1-F) \tag{1}$$

---

(1) T Titani, S Nakata and A Kanome, *Bull Chem Soc Japan* **17,** 288 (1942)

(2) N Morita and T Titani, *Bull Chem Soc Japan* **13,** 357 (1938)

(3) C A Bank, *J Inorg Nucl Chem* **7,** 195 (1958)

(4) D W Breck, W G Eversole, R M Milton T B Reed and T L Thomas *J Amer Chem Soc* **78,** 5963 (1956)

(5) H McKay, *Nature, London* **142,** 997 (1938), *J Amer Chem Soc* **65,** 702 (1943)

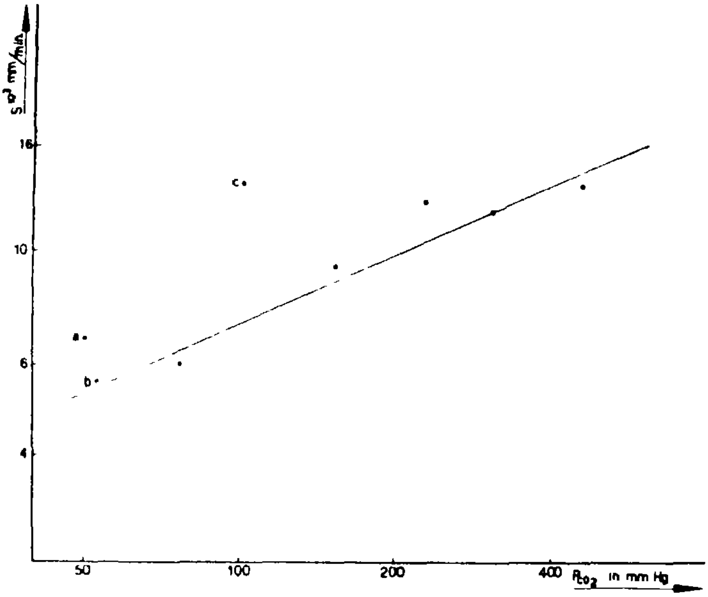


Fig 1a — Dependence of rate on CO_2-pressure at 820°C
Calculated slope 0 45 ± 0 10
a and c are experiments on a freshly prepared surface Experiment (b) is performed immediately after (a)

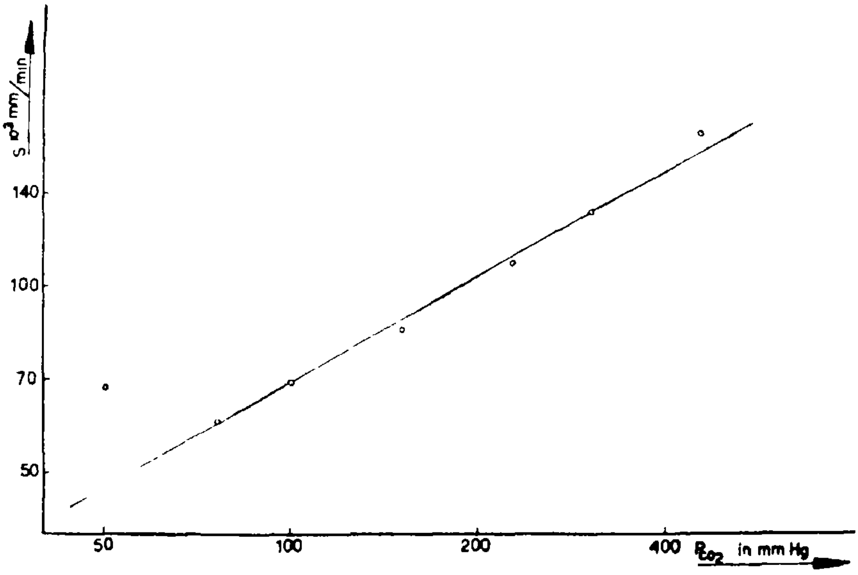


Fig 1b —Dependence of rate on CO_2-pressure at 900°C
Calculated slope 0 59 ± 0 02

F is the exchange fraction

$$F = \frac{x_t - x_0}{x_\infty - x_0}$$

Further discussion of these equations is given in the previous paper. After each experiment the ^{18}O content of the O_2 and CO_2 were determined by mass spectrometric analysis. The exchange fraction F was calculated from the values of x_t, x_0 and x_∞. By substitution of this fraction F in expression (1) the rate of exchange S was obtained. Exchange times were chosen in such a way that an exchange fraction was obtained with $0.10 < F < 0.30$.

The results are reported in Figs 1–2. The assumption of an equal distribution of oxygen-18 over both species CO_2 and O_2 at $t = \infty$ is justified by the data of UREY (6). In all these experiments no measurable amount of ^{18}O exchanged with the surface oxygen. The dependence of the exchange rate S upon reactant concentrations is given by the empirical formula

$$S = k\, p_{CO_2}{}^m\, p_{O_2}{}^n$$

The values of the exponents m and n, obtained from the plots in Figs 1–2, are given in Table 1. Calculations have been made by applying the method of least squares. It appears from these data that no change in the dependence of rate on pressure occurs between 820 and 900°C.

TABLE 1. VALUES OF THE EXPONENTS m AND n

Temp (°C)	Exponent m	Exponent n
820	0.45 ± 0.10	0.49 ± 0.06
900	0.59 ± 0.02	0.49 ± 0.04

TABLE 2. INFLUENCE OF PACKING ON THE RATE OF EXCHANGE (surface to volume ratio increased thirty eight-fold)

Temp (°C)	p_{CO_2} (mm)	p_{O_2} (mm)	Ratio of rates in packed and unpacked vessels
820	285	225	18
820	308	244	17
850	309	249	14
850	311	249	16
850	324	259	16
900	260	347	7
900	316	252	10

The question arises whether the increase in the exchange rate found on packing the reaction vessel with crushed quartz is the same for the whole temperature range. The results are reported in Table 2. At first glance the factors "packed/unpacked"

---

(6) H. C. UREY, *J. Chem. Soc.* 562 (1947).

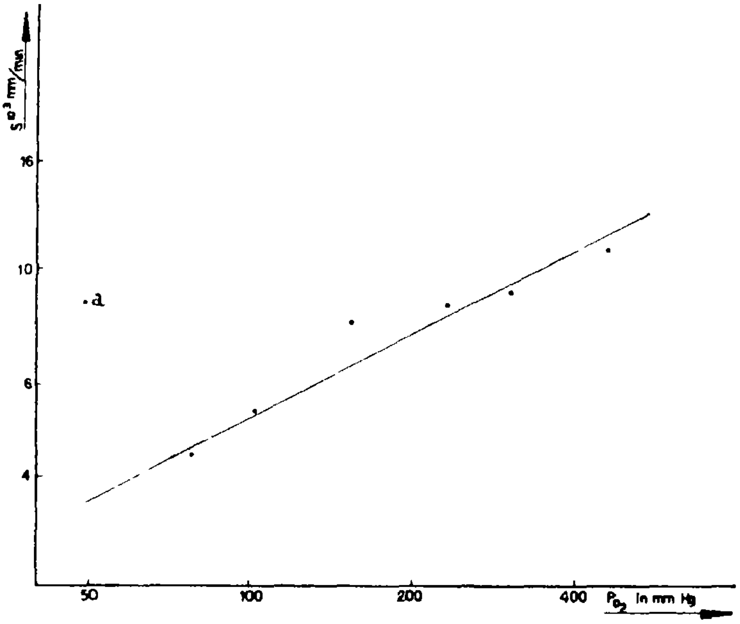


FIG 2a Dependence of rate on O_2-pressure at 820 °C
Calculated slope 0.49 ± 0.06
The point "a" is from the first experiment of a series performed after baking the reaction vessel. These first experiments used to show a relatively high reaction rate

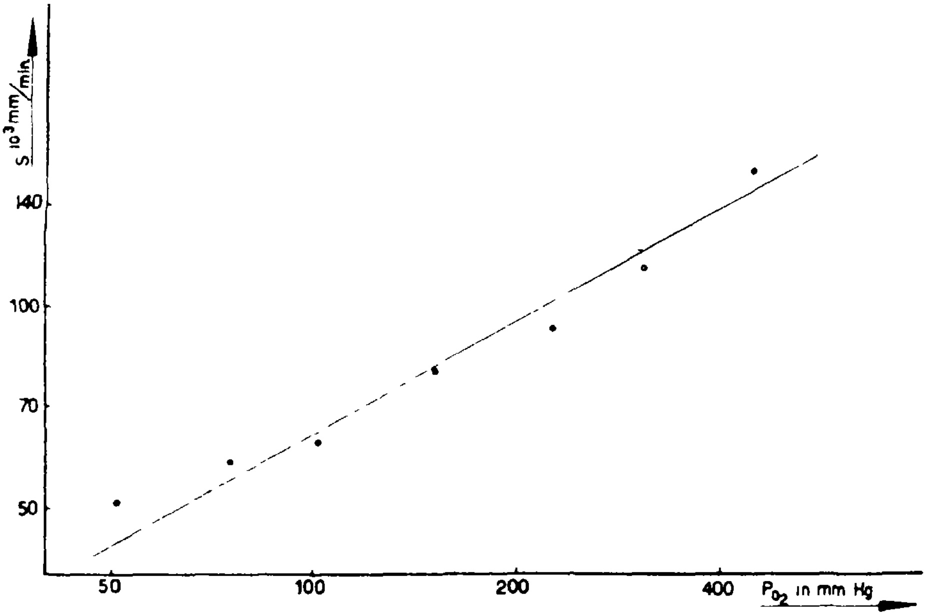


FIG 2b – Dependence of rate on O_2-pressure at 900°C
Calculated slope 0.49 ± 0.04

give the impression that at lower temperatures the reaction is distinctly more governed by the surface. However, at 820°C the accuracy of the values for the factor "packed/unpacked" is rather low in comparison with those at 850°C and 900°C. This is brought about by the great relative error in the fractional exchange (F = 0.03 ± 50 per cent) measured in the unpacked vessel. The same error calculated for the F-values at 850 and 900°C amounts to 20–25 per cent. The factors mentioned in Table 2 are then no indication for a striking difference in behaviour of the exchange reaction over the temperature range involved.

In Table 3 some data about oxygen exchange between the gases and the quartz in a packed vessel are reported. The composition and pressure of the gas mixture did not change during the experiments.

TABLE 3. OXYGEN EXCHANGE WITH THE QUARTZ IN A PACKED VESSEL

^{18}O content O_2 at $t = 0$: 0.795% ^{18}O content CO_2 at $t = 0$: 0.200%

Temp (°C)	p_{CO_2} (mm)	p_{O_2} (mm)	Time (min)	^{18}O-loss (%)
820	288	230	201	--
820	335	269	202	--
850	315	252	153	13
850	341	273	180	15
900	252	336	134	27
900	314	251	151	21

The numbers mentioned in the column '^{18}O-loss' give the percentage of the total amount of ^{18}O above natural level in the gases that has been lost to the surface.

DISCUSSION

From the data in Table 1 we conclude that for the whole temperature range 820–900°C the rate of exchange in the system CO_2–O_2 may be expressed by

$$S = k\,p_{CO_2}^{0.5}\,p_{O_2}^{0.5}$$

The surface layer of the quartz lattice probably plays an important part. Exchange measurements with the particular gases have indicated that a decrease of the original ^{18}O-content could only be explained if there is an interaction with the surface oxygen.

A more detailed insight into this mechanism may follow from considerations of GREAVES and LINNETT(7) about the recombination of oxygen atoms at quartz surfaces, which lead to the conclusion that ^{18}O can be inserted into the surface. An exchange of this ^{18}O with natural carbon dioxide that strikes the surface may occur. Further, we suppose an exchange can take place in which both molecules are adsorbed independently or by collision of a CO_2-molecule from the gas phase with O_2 adsorbed at the surface or inversely.

---

(7) J. C. GREAVES and J. W. LINNETT, *Trans. Faraday Soc.* **55**, 1355 (1959).

As can be seen from the data in Table 3, at 850°C and 900°C an exchange of oxygen between the gas and the surface has been measured in a packed vessel. We reported in our paper about CO/CO_2 exchange the occurrence of oxygen exchange with the quartz only at 900°C. Therefore, it seems justified to ascribe the exchange with the surface oxygen in CO_2/O_2 mixtures at 850°C, to oxygen exchange between the O_2 and the surface. So a CO_2/O_2 exchange mechanism involving the oxygen of the surface is certainly probable. Nevertheless, we believe the complexity of the surface results in a superposition of particular exchange processes.

Acknowledgements. We are indebted to Professor Dr. J. A. A. Ketelaar for discussions and helpful suggestions. We also thank Professor Dr. J. Kistemaker and Dr. A. E. de Vries for their stimulating interest. Mr. F. I. Monterie kindly performed the mass analyses.

This work is part of the research programme of the Stichting voor Fundamenteel Onderzoek der Materie (Foundation for Fundamental Research on Matter) and has been made possible by financial support from the Stichting Z.W.O. (Netherlands Organisation for Pure Scientific Research).

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 683 to 690. Pergamon Press Ltd. Printed in Northern Ireland

STUDIES ON PHOSPHORUS SULPHIDES

K. MOEDRITZER* and J. R. VAN WAZER
The Monsanto Chemical Co., Research and Engineering Division, St. Louis, Missouri

(*Received* 1 *November* 1961)

Abstract—Between S/P mole ratios of 0.75 and 3.50 in the phosphorus-sulphur system, quenching of melts gave completely amorphous compositions for S/P ratios of 1.0 and 1.25 (both viscous gums) and 3.0 and 3.5 (both brittle glasses). ^{31}P nuclear-magnetic-resonance (n.m.r.) spectra of the viscous liquids (heated sufficiently to avoid line broadening) show that, for S/P = 1.0, 59 per cent of the total phosphorus and, for S/P = 1.25, 33 per cent of the total phosphorus is present as the P_4S_3 bird-cage molecule. On the other hand, viscosity data indicate that macromolecules are present in melts for which S/P $\geq$ ca. 1.8. The rates of dissolution of the various crystalline, amorphous and partially amorphous phosphorus sulphides in *n*-butanol were measured and are interpreted on a per-unit-area basis. N.m.r. spectra of the solutions resulting from reaction of the butanol with the phosphorus sulphides show the presence of many phosphorus compounds.

ALTHOUGH the crystalline phosphorus sulphides have been well characterized,$^{(2)}$ the amorphous phosphorus sulphides have not been investigated since the early days of chemistry. The large-volume industrial usage of phosphorus pentasulphide has engendered interest in the amorphous phosphorus sulphides since variations in the reactivity of commercial phosphorus pentasulphide have been ascribed not only to the presence of several crystalline forms of P_4S_{10} but also to a variable content of several percent of amorphous material. In many of the commercial applications of phosphorus pentasulphide it is reacted with alcohols, and we have employed nuclear magnetic resonance in this paper to explore the products from such reactions.

This paper is the second$^{(1)}$ of several studies carried out in our laboratories directed towards the elucidation of phosphorus-sulphur chemistry.

EXPERIMENTAL DETAILS

Preparation of chemicals. Phosphorus sesquisulphide, P_4S_3, tetraphosphorus heptasulphide, P_4S_7, and phosphorus pentasulphide, P_4S_{10}, were purchased from Fisher Scientific Company. In addition, a sample of the slowly reactive grade of phosphorus pentasulphide manufactured by Monsanto was also employed. Tetraphosphorus pentasulphide, P_4S_5, was made according to the literature.$^{(3)}$ All of these crystalline phosphorus sulphides were recrystallized from boiling carbon disulphide in a soxhlet extractor under a nitrogen atmosphere with moisture excluded. In this process, the crude phosphorus sulphide was placed in an extraction thimble and the crystals were formed in the boiling flask of the extractor—overnight in the case of P_4S_3 and after a period of two weeks for the most insoluble of the crystalline phosphorus sulphides, P_4S_7. All solvents and other reagents were CP grade.

The quickly quenched phosphorus sulphides were made by combining recrystallized P_4S_3 with Baker and Adamson precipitated sulphur so as to have the following S/P mole ratios: 0.75, 1.00, 1.25, 1.75, 2.50, 3.00 and 3.50. These mixtures were sealed, under a nitrogen atmosphere, in 7 mm o.d.

---

* On leave of absence from the Inorganic Chemicals Division of Monsanto, July 1961–62.

[1] L. MAIER and J. R. VAN WAZER, *J. Amer. Chem. Soc.* **84**, 3054 (1962).

[2] J. R. VAN WAZER, *Phosphorus and Its Compounds*, Vol. 1, pp. 289–308. Interscience, New York, (1958). Also see A. R. PITOCHELLI and L. F. AUDRIETH *J. Amer. Chem. Soc.* **81**, 4458 (1959).
R. BOULOUCH, *C.R. Acad. Sci., Paris* **138**, 363 (1904); W. D. TREADWELL and C. BEELI, *Helv. Chim. Acta* **18**, 1161 (1935).

silica tubes 30 cm long. The tubes were then held in a furnace at 350° until a clear melt ensued. Quenching was achieved by dropping them immediately into a well-stirred bath of finely crushed ice and water. Preliminary experiments indicated that the same final results were obtained whether the melts had been held at 350° for a long or short period of time. In all cases, there was a small amount of char on the walls of the tubes due to organic materials present in both the sulphur and the phosphorus sesquisulphide. In an exploratory study, an S/P ratio of 0.50 (made by mixing P_4S_3 with red P) was heated over a Bunsen burner to give a single-phase liquid which, upon quenching, separated into a waxy solid spontaneously flammable in air (white P) and a phosphorus sulphide exhibiting the X-ray diffraction pattern of P_4S_3.

Physical measurements. The ^{31}P nuclear-magnetic-resonance (n.m.r.) studies were carried out with a Varian high-resolution spectrometer utilizing a V-4311 RF probe operating at a frequency of 24.288 Mc/s. The magnet (operated at ca. 14,100 G) was equipped with the usual superstabilizer, temperature control, homogeneity shim coils, etc. Except for the butanol solutions which were measured in 15 mm tubes after partial evaporation of the butanol, 5 mm tubes were used to hold the samples in the n.m.r. spectrometer. Referencing was achieved by dropping a capillary tube containing 85 per cent H_3PO_4 into the sample. Chemical shifts are presented in p.p.m. of the magnetic field, using 85 per cent orthophosphoric acid as reference, with negative shifts being downfield and an accuracy of ca. ±2 p.p.m.

The X-ray measurements were made on a Norelco diffractometer, using copper K_α radiation and a nickel filter to get a wave length of 1.541 Å. During the X-ray measurement, the sample was protected from the atmosphere by a 25 mil Mylar film. Viscosities of a number of melts having S/P ratios in the range of 1.79–2.75 were measured in several Monsanto laboratories by (1) a Brookfield viscometer from which the rotating spindle was suspended by a long rod and (2) a capillary suction-viscometer of the type used on sulphur.(4) The viscosities of the amorphous material for which S/P = 1.00 and 1.25 were obtained on a Haake Rotovisko fitted with a thermostated plate-and-cone measuring head. Considerable difficulty was experienced in determining the viscosity of the viscid gum for which S/P = 1.25. This was primarily due to rapid crystallization of P_4S_3 between the plate and cone and to reaction with the atmosphere at their edges because of the elevated temperatures employed.

The kinetics of dissolution in n-butanol was measured in test tubes which were agitated in a thermostated water bath (25, 39 and 75°) or in refluxing n-butanol (115°) by a Burrell wrist-action shaker. The shaking was adjusted, in the case of particulate material, so that the particles were continuously swept through the solution and, in the case of viscid samples, so as to cause the butanol phase to flow rapidly over the surface of the viscid material at the bottom of a special flat-bottomed test tube without deforming the interface. During these studies, dry nitrogen was led into the test tube to sweep out the evolved H_2S which was absorbed in a sodium acetate-buffered solution of zinc chloride. After addition of iodine to the resulting zinc sulphide, a titration was carried out with thiosulphate.(5)

RESULTS AND CONCLUSIONS

Amorphous phosphorus sulphides

Since products completely amorphous by X-ray diffraction could be obtained by our rapid-quenching procedure only at S/P mole ratios of 1.0, 1.25, 3.0 and 3.5, it is apparent that the crystalline species P_4S_{10},* P_4S_7 and P_4S_3 crystallize very rapidly from the melt. The amorphous compositions at S/P mole ratios of 3.5 and 3.0 are brittle glasses, whereas those at S/P = 1.25 and 1.00 are viscid gums at room temperature. The viscosities of these latter two compositions are presented in Fig. 1 as a function of temperature. This figure also presents the available data on S-P melts, including pure molten sulphur.(4) The phosphorus sulphides having S/P mole ratios in the range from 2.0 to 3.0 exhibit maxima in viscosity with changing temperature, as has been found with pure sulphur These maxima are displaced to higher temperatures and lower viscosities with increasing phosphorus content Qualitative evidence indicates that there is a regular decrease in the height of the maxima, with a corresponding increase in the temperature at which it appears, as the composition ranges from pure sulphur to an S/P mole of ca 2

---

* In a previous study,(1) amorphous P_4S_{10} was obtained by quenching between copper chill-plates.

(4) R. F. BACON and R. FANELLI, *J. Am. Chem. Soc.* **65**, 639 (1943). Also see R. E. POWELL and H. EYRING, *ibid.* **65**, 648 (1943).

(5) W. RIEMAN, J. D. NEUSS and B. NAIMAN, *Quantitative Analysis*, p. 279. McGraw-Hill, New York (1942).

The most extensive studies on the viscosity of molten phosphorus sulphides have been carried out at an S/P ratio 2 5, where it is found that additives which significantly reduce the viscosity of pure sulphur have little effect From an experimental

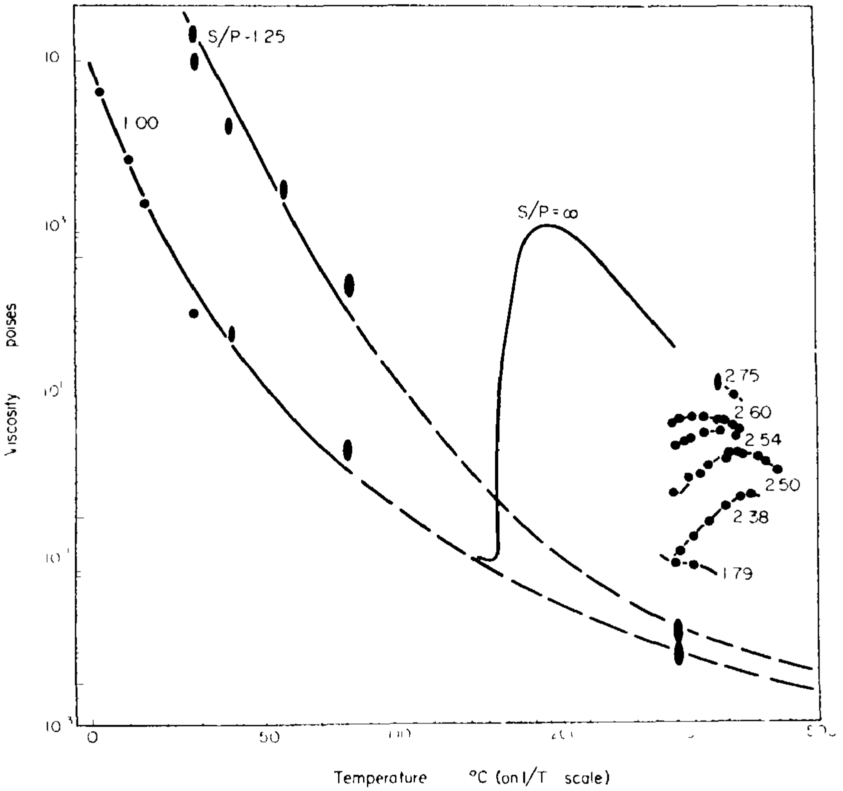


FIG 1 —Viscosity of various phosphorus sulphides

viewpoint, the major variations of viscosity with time are due to preferential loss of phosphorus due to vapourization—a process which leads to a pronounced continuing rise in viscosity of molten phosphorus pentasulphide The rate of this rise seems to be decelerated by exposure to light

At all temperatures studied, the fluid phosphorus sulphides appeared to exhibit Newtonian flow This probably means that molecular reorganization at temperatures in the range of 300–500° is rapid with respect to the jumps made by molecule segments during flow

N m r studies on warmed samples of the two phosphorus sulphides which were produced as gums at room temperature showed 59 per cent of the total phosphorus is present as the P_4S_3 molecule in the composition for which S/P = 1 00, and 33 per cent as P_4S_3 in that for which S/P = 1 25 A number of other resonance peaks were seen in these spectra* but at such low intensities that interpretation in terms of molecular constitution was impractical.

From these data and the findings of previous workers(1–6) it is seen that amorphous phosphorus sulphides undergo rapid structural reorganization at temperatures of several hundred degrees with this reorganization involving (1) long S–S chains, (2) S–S chains with branches and crosslinks through phosphorus atoms, (3) sulphur rings and (4) phosphorus sulphide cage-molecules. It is qualitatively apparent that the long chains are present in insignificant amounts for S/P < ca. 1.8 and that the P_4S_3 cage-molecule predominates at ca. 0.6 < S/P < ca. 1.2.

Kinetics of alcoholysis

The various phosphorus sulphide compositions, both quenched and recrystallized, were reacted with n-butanol in amounts equivalent to a one molar solution in phosphorus upon complete dissolution. The solids were ground so as to pass through a 50-mesh and be retained upon a 60-mesh screen, and the resulting powder was agitated in the butanol throughout the reaction. In the case of the two phosphorus sulphide gums (S/P = 1.00 and 1.25) dissolution was carried out at a level-surface interface. In order to compare these two situations, a constant rate of dissolution per unit area was assumed for a given preparation and temperature. A further assumption for the powdered solids of equal-sized spheres having a density of 2.1 g cm^{-2} and an original diameter of 275 μ (screen cut of 50–60 mesh) led to the following equation for the unit rate of alcoholytic dissolution, γ, in g cm^{-2} min^{-1}:

$$\gamma = (2.9 \times 10^{-2}/t)(1 - \sqrt[3]{(w_t/w_0)}) \tag{1}$$

where t is the time in min. and w_t and w_0 are the weights in grammes at time t and time zero, respectively.

The experimental data are reported in Table 1, from which it can be seen that there is a gradual decrease in γ with diminishing S/P ratio. It should be noted that crystalline samples of phosphorus pentasulphide (S/P = 2.50) exhibited a five-fold difference in γ. Moreover, the kinetic data on sample No. 2 did not fit equation (1) very well, as the value of γ was found to diminish appreciably with increasing t. Microscopic inspection showed that this carefully sized preparation contained a large amount of agglomerated feathery crystals so that the initial area was estimated greater than that of sample No. 1, which consisted of blocky crystals with a much smaller proportion of agglomerates. Because of rapid dissolution of the agglomerated feathery crystals at the beginning of a run, the over-all dissolution rate of sample No. 2 of P_4S_{10} decreased with time as measured by γ.

From microscopic examination, a very rough estimate could be made of how much greater the gross area of a given preparation would be as compared to even-sized blocky crystals or fracture fragments By multiplying the value of γ by this area factor, the corrected rates shown in the last column of Table I were obtained These corrected rates indicate that in all cases, except for S/P 1 75, the quenched product dissolves more rapidly than the crystals of the same composition

---

* For S/P = 1.00 the following n.m.r. resonances in addition to those(2) corresponding to the P_4S_3 molecules were seen: −147 p.p.m. (corresponding to ca. 5 per cent of the total phosphorus), −143 (4%), −137 (6%), −133 (5%), −128 (5%), −116 (7%), −66 (4%), and −61 p.p.m. (5%). For S/P = 1.25, the following additional resonances were seen: −262 p.p.m. (8%), −232 (13%), −221 (4%), −181 (12%), −166 (3%), −152 (5%), −142 (4%), −138 (3%), −108 (7%), and −58 p.p.m. (8%).

(6) H. Specker, *Angew. Chem.* **65**, 299 (1953); *Kolloid-Z.* **125**, 106 (1952); *Z. Anorg. Chem.* **261**, 116 (1950); J. A. Prins and J. Schenk, *Plastica* **6**, 216 (1953); J. C. Pernert, U.S. Pat. 257720 (1951); Brit. Pat. 667893 (1952, assigned to Oldbury Electrochem. Co.). Also see the discussion of these papers in Reference 2.

The biggest difference between the quenched and crystalline preparations occurs at S/P - 1 25, where the quenched sample was completely amorphous It should be noted that for each S/P ratio where the quenched sample exhibited an X-ray diffraction pattern, this pattern was quite similar to that of the recrystallized sample of the same composition The reversal for S/P 1 75 from the usual case in which

TABLE I –RATES OF DISSOLUTION OF PHOSPHORUS SULPHIDES UPON REACTION WITH N-BUTANOL *

S P Atomic ratio	State	γ_2	Estimated area factor (f)	Corrected rate at 25 (γ f) 10^{4} g cm ^{2} sec ^{1}
3 50	Amorphous	1 8 10^{3}	1 8	10 0
3 00	Amorphous	0 9 10^{3}	2 5	4 0
2 50	Quenched[†]	0 7 10^{3}	1 9	4 0
	Recrystallized No 1	0 5 10^{4}	2 0	0 3
	Recrystallized No 2	2 5 10^{4}	10 0	0 3
1 75	Quenched[†]	2 3 10^{5}	1 8	0 1
	Recrystallized	1 1 10^{4}	1 3	0 9
1 25	Amorphous	3 10^{5}	1 0	0 3
	Recrystallized	3 10^{6}	1 3	0 02
1 00	Amorphous	7 10^{5}	1 0	0 7
0 75	Quenched[†]	2 10^{6}	1 7	0 01
	Recrystallized	3 10^{7}	1 3	0 002

* Concentration in all cases is 1 g atomic wt of P, 1000 ml of butanol

[†] Approximately the same X-ray diffraction pattern as the recrystallized sample of the same composition

the quenched material is the more reactive probably indicates that there is a pronounced difference in molecular structure between the amorphous part of the quenched material and the P_4S_7 bird-cage molecule It is interesting to note that this is the composition where the maximum in melt viscosity disappears (see Fig 1) Perhaps the amorphous constituent is a three-dimensional network polymer at the gel points

A priori, it would be expected that a completely amorphous chemical system should exhibit a monotonic change of properties such as rate of solvolysis with composition However, assuming that the experimental interpretative techniques used here give a valid comparison of powdered glasses with gums, it would appear that there is a flat minimum in the rate of alcoholytic dissolution of the completely amorphous phosphorus sulphides at an S/P ratio around 1 5-2 0

The experiments on the temperature coefficient of alcoholytic dissolution have led to the conclusion that the process is essentially temperature independent for crystalline P_4S_3 and P_4S_5 but has an activation energy around 5–10 kcal/mole for crystalline P_4S_7 and P_4S_{10}

TABLE 2.—REACTION PRODUCTS FROM ALCOHOLYSIS OF PHOSPHORUS SULPHIDES IN n-BUTANOL
(1 g atomic wt of P/1000 ml of butanol reacted at 25° except where noted)

Reagents												
S/P mole ratio		3.50	3.00	2.50		1.75		1.25		1.00	0.75	
Type		Glass	Glass	P_4S_{10}	Quenched crystalline	P_4S_7	Quenched crystalline	P_4S_5	Viscous gum	Viscous gum	P_4S_3	Quenched crystalline
Products												
Moles H_2S evolved/4P		1.95	2.24	0.88	1.80	1.33	1.52	2.29[a]	1.92	0.96	0.62[a]	0.36[a]
Ppt (vol % and colour)		10%, white	5%, white	none	none	none	none yellow	6%, yellow	45%, orange	45%, yellow and white	25%, yellow	5%, white
Sol of ppt in CS_2		sol	sol					insol	insol	insol	insol	insol
Approx % of P (to ±3 units) corresponding to observed n m r peaks	Chem shift (p p m)											
	−101					13						
	−96[b]			8				18				
	−92[c]					29	33					
	−86[d]	100	100	62	93	10					14	
	−81[e,f]			6	7		20	14				
	−72						11					
	−66[g]			15		16	17	15				
	−60[e,h]			9		10	8	17			18	
	−56[i]						11					
	−36					6						
	−28							10				
	−23[j]							12			23	
	−20[k]					5					13	
	−10					7						
	−1[m]								100	100		100
	6							14			18	
	+9[k]										14	
	+13[n]					4						

[a] At 114° [b] Possibly $(BuO)_2(BuS)PS$ [c] Probably $(BuS)_3PS$ [d] $(BuO)_2PS_2H$ [e] Possibly $(BuO)_2P(H)S$ [f] More probably $[(BuO)_2PS]_2S_n$ for $n \geqslant 1$ [g] Probably $(BuO)_3PS$ [h] Probably $(BuS)_3PO$ [i] Probably $(BuO)_2POSH$ [k] Possibly $(BuO)_2P(H)O$ [l] $(BuO)_3PO$ [m] $[(BuO)_2PO]_2O$

Products from alcoholysis

The experimental data obtained on the various recrystallized and quenched preparations dissolved in sufficient n-butanol to give, upon complete dissolution, a solution one molar in phosphorus are presented in Table 2. The first two lines of this table describe the phosphorus sulphide starting-materials, and the next line gives the amount of H_2S evolved during alcoholysis (at 25° except when noted at 114°). The fourth and fifth lines in the table describe any precipitate formed, and the remainder of the table is devoted to the n.m.r. data obtained on the final solutions after concentration by room-temperature evaporation of the butanol. When this study was initiated, it was hoped that, from a measure of the H_2S evolved and our present knowledge of n.m.r. chemical shifts of phosphoric and thiophosphoric esters and acid esters, it would be possible to identify the alcoholysis products. However, more detailed study of the situation has shown this to be as yet impossible, mainly because as many as seventy-four compounds based on a single phosphorus atom might result from these reactions and there are many more possible compounds containing more than one phosphorus atom. In addition, overlapping of n.m.r. resonance peaks is to be expected.

The simplest products result from alcoholysis of the completely amorphous compositions. For S/P ratios of 3.50 and 3.00, the sole products from alcoholysis are a colloidal precipitate of sulphur and the alcohol-soluble compound, $(C_4H_9O)_2PS(SH)$. For the amorphous compositions exhibiting S/P ratios of 1.25 and 1.00, the only alcohol-soluble product is the ester $(C_4H_9O)_3PO$, but there is a considerable amount of phosphorus-containing precipitate, amorphous to X-rays and insoluble in common solvents. This is thought to be an infinite-network polymer based on phosphorus, sulphur, and oxygen, with some butyl groups at terminal points in the structure.

Although the quenched samples corresponding to S/P = 2.50, 1.75 and 0.75 exhibited X-ray patterns quite similar to those obtained on recrystallized P_4S_{10}, P_4S_7, and P_4S_3, respectively, there is a pronounced difference in the products of alcoholysis. Thus, alcoholysis of recrystallized P_4S_{10} led to five n.m.r. resonance peaks, with ca. 60 per cent of the total phosphorus as the molecule $(C_4H_9O)_2PS(SH)$. On the other hand, the quenched material of the same over-all composition had ca. 90 per cent of the total phosphorus present as $(C_4H_9O)_2PS(SH)$, with only one other material present in detectable amount. For S/P = 0.75, the alcohol-soluble products of alcoholysis of recrystallized P_4S_3 showed six n.m.r. peaks of approximately equal intensity, whereas, for the quenched material, the only alcohol-soluble product was the $(C_4H_9O)_3PO$. It should also be noted that about five times as much amorphous precipitate, insoluble in common solvents, was produced from recrystallized P_4S_3 as from the same composition quenched from the melt.

Discussion

In spite of technical difficulties preventing a thorough interpretation of the findings, the experiments described herein give a number of clues to the molecular constitution of the amorphous phosphorus sulphides. The presence of P_4S_3 bird-cage molecules in the quenched gums, the disappearance of the maximum in melt viscosity, the faster alcoholysis of crystalline P_4S_7 as compared to the quenched material, the apparent minimum in the extrapolated rate of alcoholysis of the completely amorphous phosphorus sulphides as well as the variation in products of alcoholysis with S/P ratio are all consistent with the idea that increasing incorporation of phosphorus into quenched polymeric sulphur leads first to branching and cross-linking and then to gradual breakdown of the polymeric structures through formation of small bird-cage molecules. At elevated temperatures, this picture is complicated by rapid reorganization of the molecular structures.

As more information is gathered concerning the ^{31}P n.m.r. response of the various phosphoric and thiophosphoric esters, some of the findings here will be subject to further interpretation. This coupled with new and different experimental approaches will some day clarify phosphorus–sulphur chemistry to the extent already achieved for phosphorus–oxygen chemistry.

Acknowledgement—We wish to thank L. MAIER for carrying out preliminary studies on the preparation of amorphous phosphorus sulphides and their alcoholysis. The data presented in Fig. 1 on molten phosphorus sulphides were obtained by M. L. SALUTSKY, J. W. CROSS, C. R. BOSTIC, H. E. ULMER and W. I. TUCKER. We also wish to acknowledge the help of V. MARK, A. F. LIPPMAN and R. FREEMAN in obtaining the n.m.r. data on which the tentative assignments of Table 2 were based.

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 691 to 696. Pergamon Press Ltd. Printed in Northern Ireland

INVESTIGATION OF THE CHEMISTRY OF PENTAVALENT NEPTUNIUM

YU. A. ZOLOTOV and I. P. ALIMARIN
V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry,
Academy of Sciences of the USSR, Moscow, USSR

(*Received* 4 *November* 1962)

Abstract—The formation of complex compounds of Np(V) in solutions of oxalic, tartaric, citric and ethylenediaminetetraacetic acids has been investigated by an ion exchange procedure. Several complexes have been shown to exist and their composition and stability constants determined. A qualitative spectrophotometric study has shown Np(V) forms complexes with some other substances. The ability of the NpO_2^+ ion to form complexes appears to exceed that expected for a large singly charged cation. The extraction of Np(V) chelates with thenoyltrifluoroacetone, acetylacetone, 1-nitroso-2-naphthol, cupferron and 8-hydroxyquinoline has been studied. Chelates of Np(V) with TTA and 1-nitroso-2-naphthol have been shown to be readily extracted at pH 7–10 by solutions of the reagents in active oxygen-containing solvents, especially in n-butyl and other alcohols. The nature of the solvent markedly affects the extraction. The properties of NpO_2^+ have been compared with those of the ions of other pentavalent actinides and an analogy between Np(V) and Am(V) and between U(V) and Pu(V) noted.

The pentavalent state of neptunium is chemically the most interesting. Neptunium (V) is more stable, not only than other valence states of neptunium but than all other pentavalent actinides of the series U–Am. The NpO_2^+ ion has no well known analogues in the periodic system and is effectively unique though in some respects similar to the doubly charged ions of the hexavalent actinides. We have investigated the chemical properties of pentavalent neptunium by means of its isotope ^{239}Np. In some cases use was made of the long lived ^{237}Np.

This paper briefly reports on the results of our investigations, some of which are published in detail in the Russian literature.

THE FORMATION OF Np(V) COMPLEXES IN AQUEOUS SOLUTIONS

The pentavalent actinides of the series U–Am, forming in aqueous solutions ions such as MeO_2^+, have among all the valence states of these elements the least tendency to complex formation. It does not seem however to be as weak as would be expected for large singly charged cations. We have investigated the coordination of NpO_2^+ with oxalic, tartaric, citric and ethylenediaminetetraacetic acids by means of an ion exchange procedure.

Experimental

Neptunium (V) solution has been prepared by treatment of an ether extract containing neptunium (VI) with cold 0.1 M hydrazine nitrate solution in nitric acid. Then neptunium (V) has been extracted with 1-nitroso-2-naphtholate at pH 9 and stripped with 1 M perchloric acid solution.

The distribution of traces of Np(V) was studied under static conditions between a solution in 0.5 M NH_4ClO_4 and the cation exchanger CU-2 (similar in properties to Dowex-50) in the ammonium form both in the presence of the coordinating substance and without it. The ionic strength was maintained constant by means of NH_4ClO_4 $HClO_4$ and NH_4OH, the temperature was 20 + 2° The solutions were shaken with the cation exchanger during 4-6 hours and the equilibrium pH determined with a glass electrode The concentration of ${}^{239}Np$ was evaluated by conventional radiometric procedures The data obtained were mainly treated by Shubert's method

Results

In oxalate solutions of Np(V) at pH 2-5 the co-ordination compounds $NpO_2HC_2O_4$, $NpO_2C_2O_4$ and $NpO_2(C_2O_4)_2^{3}$ are formed, their stability constants being 5 0 10^{2}, 1 1 10^{4} and 2 3 10^{7}, respectively The two latter compounds had been previously reported by GRUEN and KATZ(1) In tartrate solutions at pH 3 2 6 2 the complexes NpO_2H Tart, NpO_2 Tart , NpO_2 $Tart_2^{3-}$ and, presumably, NpO_2 $Tart_3^{7}$ are formed their stability constants being 2 3 10^{2}, 2 1 10^{2}, 2 0 10^{4} and 1 5 10^{6}, respectively With citric acid at pH 4 3 5 2 the compounds NpO_2 Cit^{2-} and NpO_2H Cit are formed with stability constants 4 7 10^{3} and 4 9 10^{2}, respectively In solutions of EDTA at pH 5 3-5 6 NpO_2Y^{3-} is formed whose stability constant 4 9 10^{9} is close to the value obtained by GELMAN and MEFODYEVA(2) More detailed data are given in papers(3,4) published in collaboration with MOSKVIN and MAROV

Miscellaneous data on co-ordination

The changes in the absorption spectrum of pentavalent ${}^{237}Np$ allow one to conclude that the NpO_2 ion co-ordinates with trioxyglutaric, salicylic, 2,3-dioxyterphthalic, acetic, and phthalic acids, as shown by the spectra of Np(V) in citric acid solutions in Fig 1 The ionic strength changes very little with pH changes (the concentration of the complexing agent was constant) Other spectra are given in paper (5)

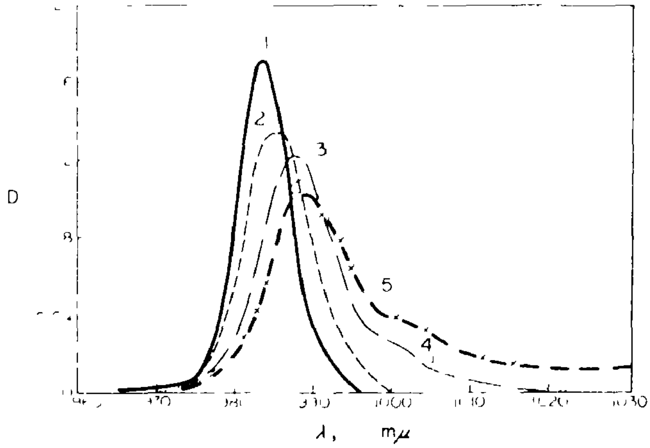


FIG 1 —Absorption spectrum of aqueous solution of Np(V) in the presence of citric acid 1 pH 0 9, 2—pH 3 5, 3—pH 5 1, 4—pH 5 7, 5 pH 6 1

(1) D M GRUEN and J J KATZ, *J Amer Chem Soc* **74,** 2103 (1952)

(2) A D GELMAN and M P MEFODYEVA, *Dokl Akad Nauk SSSR* **124,** 815 (1959)

(3) YU A ZOLOTOV, I N MAROV and A I MOSKVIN *Zh Neorg Khimii* **6,** 1055 (1961)

(4) A I MOSKVIN, I N MAROV and YU A ZOLOTOV, *Zh Neorg Khimii* **6,** 1813 (1961)

(5) YU A ZOLOTOV and YU P NOVIKOV, *Zh Neorg Khimii* **4,** 1693 (1959)

Discussion

The data obtained show that neptunium (V) has a rather strong tendency to form co-ordination compounds. The comparison of the stability constants of the NpO_2^+ complexes with those of other elements having an identical number of the same ligands[(6)] leads to the conclusion that the constants for NpO_2^+ are near to the corresponding constant, for doubly charged cations, such as Mg^{2+}, Ca^{2+}, Co^{2+}, Ni^{2+}, as illustrated by the data for the oxalate complexes. If one neglects the effect of the structure of the electron shells and considers the ionic potentials as a measure of the ability of ions to coordinate then, bearing in mind the above analogy with doubly charged cations, it is possible to estimate the effective ionic potential of NpO_2^+, as about 2.1, which is a rather high value for a singly charged ion. This seems to follow because of the symmetric and linear structure of the ion and the nature of the Np–O bond, which causes such a redistribution of the ionic charge as to lead to the central atom acquiring a higher positive charge and the oxygen atoms some negative charge.[(7)]

EXTRACTION OF CHELATE COMPOUNDS OF PENTAVALENT NEPTUNIUM

There seem to be no data in the literature on the extraction of pentavalent actinides except for the atypical protactinium. Kooi[(8)] while studying the extraction of neptunium from nitric solutions came to the conclusion that Np(V) can be extracted in traces, say, by methyl-iso-butyl ketone at a concentration of HNO_3 higher than 5 M. However, under these conditions Np(V) disproportionates extensively to give Np(IV) and Np(VI) that are readily extracted by oxygen-containing solvents.

One could however have expected NpO_2^+ to form chelates with suitable reagents, that would be extracted by organic solvents. On the basis of the pH data for the hydrolysis of the ion and its interaction with organic acids it would be expected that the extraction of chelates of neptunium (V) would proceed at higher pH than six. We have investigated the extraction of the Np(V) compounds of thenoyltrifluoroacetone, acetylacetone, 1-nitroso-2-naphthol, 8-hydroxyquinoline, cupferron, etc. It has been shown that some chelates are well extracted at a sufficiently high pH of the aqueous solution (a pH of 7–10). The nature of the solvent used appears to be very important.

Thenoyltrifluoroacetonate

Alcohols, such as n-butyl, isoamyl, and hexyl alcohols readily extract the TTA complex at a pH of 7–9 (Fig. 2). Quantitative extraction by, say, isobutyl alcohol is effected after three consecutive extractions. Ketones such as cyclohexanone and methylethylketone also extract the neptunium complex but less readily than do alcohols. Esters such as ethylacetate and amylacetate extract neptunium almost as well as ketones. Ethers such as diisopropyl ether, halogeno derivatives of hydro-

---

[6] Y. Bjerrum, G. Schwarzenbach and L. G. Sillen, Stability Constants of Metal-ion Complexes with Solubility Products of Inorganic Substances. Part I. Organic Ligands, L., 1957. Part II, Inorganic Ligands, L., 1958.

[7] R. E. Connick and Z. Z. Hugus, *J. Amer. Chem. Soc.* **74**, 6012 (1952).

[8] J. Kooi, *Tracer Experiments on the Solvent Extraction of Neptunium and Plutonium.* Amsterdam, (1956).

carbons (1 2-dichloroethane CHCl$_3$, CCl$_4$) and hydrocarbons (benzene, heptane) fail to extract the neptunium Such an important effect of the nature of the solvent on the extraction of ^{239}Np allows one to separate Np(V) from other elements, whose complexes with TTA are extracted by benzene at the same pH's (e g from lanthanides)

The theoretical aspect of the effect of the nature of the solvent on the extraction of chelates is discussed elsewhere (9 10)

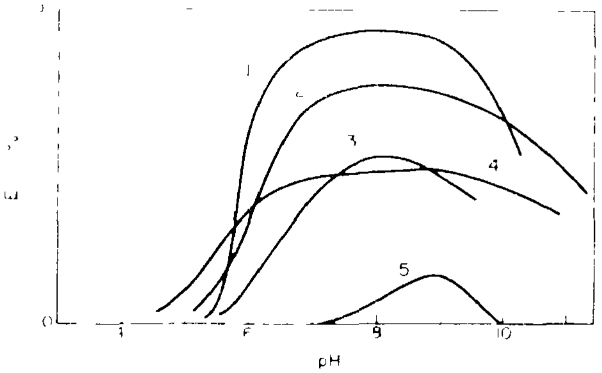


FIG 2—Dependence of the percentage of extraction of neptunium (V) thenoyltrifluoroacetonate on the nature of the solvent

1 isobutyl alcohol 2 cyclohexanon, 3 ethylacetate, 4 methylethylketone 5 amylacetate

1-Nitroso-2-naphtholate

Butyl and isoamyl alcohols extract Np(V) nitroso-naphtholate at a pH of 8 11 Other solvents such as methylethylketone amylacetate, chloroform and especially diethyl ether and benzene extract this neptunium complex less readily The extraction by alcohols is suppressed by large amounts of fluorides, phosphates carbonates, oxalates and citrates and especially by ethylenediaminetetraacetic acid In small amounts flourides, carbonates and hydrogen peroxide do not markedly affect the extraction whereas sulphates chlorides and nitrates are without any effect Extraction of the nitrosonaphtholate followed by back-extraction can be used to produce solutions of ^{239}Np(V) free from redox agents or other impurities (11 12)

Miscellaneous chelates

The 8-hydroxyquinolinate and particularly the acetylacetonate are extracted somewhat less readily The cupferronate extraction curve shows a minimum as described elsewhere (13) The dependence of the extraction on the nature of the solvent is rather similar to that of the complex with TTA

(9) YU A ZOLOTOV and I P ALIMARIN *Dokl Akad Nauk SSSR* **136**, 603 (1961)

(10) YU A ZOLOTOV and I P ALIMARIN *Radiokhimiya* **4**, 272 (1962)

(11) I P ALIMARIN YU A ZOLOTOV and F S PALSHIN *Radiokhimiya* **2**, 637 (1960)

(12) I P ALIMARIN, YU A ZOLOTOV and E S PALSHIN *Dokl Akad Nauk SSSR* **124**, 328 (1959)

(13) I P ALIMARIN, O M PETRUKHIN and YU A ZOLOTOV *Zh Analyt Khimii* **17**, 544 (1962)

NON-MONOTONOUS CHANGE OF IONIC PROPERTIES IN THE SERIES UO_2^+–AmO_2^+

There are sufficient data to indicate a regular change in chemical properties of ions of the tri, tetra and, to some extent, hexavalent actinides with increasing atomic number of the element. This can be understood by assuming the elements of the series have 5*f*-electrons and allowing for the ionic contraction. On the other hand, it is known that pentavalent neptunium differs substantially from pentavalent uranium and plutonium in being very stable in aqueous solutions, thus no smooth change of stability occurs in the series UO_2^+-NpO_2^+-PuO_2^+. This phenomenon has not been accounted for though, as noted by KATZ and SEABORG[14], and McKAY[15], the question of the stability of pentavalent neptunium is one of the most interesting in the chemistry of the actinides. It seemed therefore pertinent to carry out a more detailed comparison of the chemical properties and physical–chemical characteristics of the ions in the series UO_2^+–AmO_2^+.

The comparison of ionic properties

We have compared the electrode potentials, the entropy, the constants of the disproportionation reactions and the data on disproportionation kinetics, the tendency to hydrolysis as well as some other characteristics. This comparison has led us to the conclusion that some properties of thin ions experience a non-monotonous change with increasing atomic number of the element. One can see a marked analogy between the ions of pentavalent uranium and plutonium on the one hand, and those of pentavalent neptunium and americium on the other. This can, for instance be illustrated by the data on the difference ΔE between the potentials of the pairs V–VI and VI–V that characterise the tendency to disproportionation (Table 1) or by the data on ionic entropies (Fig. 3).

TABLE 1.—POTENTIALS FOR THE COUPLES Me (V)/Me (VI) AND Me (IV)/Me (V), AND THE DIFFERENCE IN $\Delta E = E_{V,VI}-E_{IV,V}$ FOR ELEMENTS OF THE SERIES URANIUM–AMERICIUM

Element	$E_{V/VI}$, V	$E_{IV/V}$, V	ΔE, V
U	0.063	0.58	0.52
Np	1.137	0.739	0.398
Pu	0.913	1.172	−0.259
Am	1.60	1.04	0.56

Discussion

The interpretation of these data is involved and requires special consideration. The following should, apparently, be taken into account:

(1) whether the atomic number of the element and the total number of electrons in the ion is even or odd,

---

[14] J. J. KATZ and G. T. SEABORG, *The Chemistry of the Actinide Elements*, Wiley, New York (1957).
[15] H. A. C. McKAY, *Industr. Chem.* 33, 297 (1957).

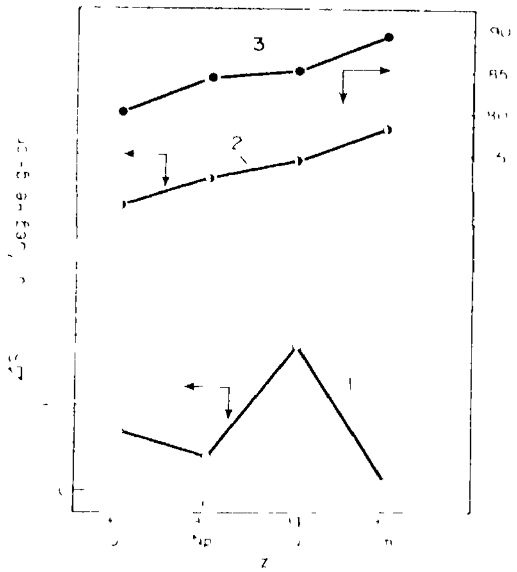


FIG. 3.—Change in the entropy of actinide ions depending on the atomic number of the element

1 MeO_2^+, 2 Me^{3+}, 3 Me^{4+}

(2) how many 5*f*-electrons are available in the central atom,

(3) whether 5*f*-electrons can participate in the formation of a covalent metal-oxygen bond and if the degree of covalency is affected by changing the charge on the nucleus and the number of 5*f*-electrons,

(4) what is the distribution of the ionic charge which can lead to an increased formal charge on the central atom

(5) whether this charge can be changed by the degree of covalency of the metal-oxygen bond

The difference in the chemical properties of the pentavalent actinide ions can be of practical value In particular, it may be used to separate elements even when these ions have no stable coexistance in solution This has been exemplified by the work of SAMARTSEVA(16), who showed that during electrolysis neptunium separates more quickly than plutonium and uranium owing to the stability of its pentavalent state

This non-monotonous change in properties of the ions of pentavalent actinides has been considered further elsewhere (17)

Acknowledgement - We are grateful to G A VOROBJEVA, YU P NOVIKOV, I N MAROV and A I MOSKVIN for their collaboration in some parts of the investigation

---

(16) A G SAMARTSEVA Isotopi i islutshenya v Khimii Moscow, 1958, p 318
(17) YU A ZOLOTOV *Radiokhimiya* 2, 192 (1960)

J Inorg Nucl Chem, 1963 Vol 25 pp 697 to 709 Pergamon Press Ltd Printed in Northern Ireland

A STUDY OF SORPTION ON ZIRCONYL PHOSPHATE AND CHANGES OF ITS PROPERTIES AT HIGHER TEMPERATURES

V Veselý and V Pekárek
The Nuclear Research Institute of Czechoslovak
Academy of Sciences, Řež near Prague, Czechoslovakia

(*Received* 22 *May* 1962, *in revised form* 19 *November* 1962)

Abstract - A method of chromatographic separation of zirconium from phosphate anion on an anion exchanger was developed for the analysis of zirconyl phosphate The ratios P/Zr in zirconyl phosphates prepared under different conditions of precipitation were determined The sorption of some 1 to 4 valent cations was investigated on different types of zirconyl phosphates heated to various temperatures By measuring the infra-red absorption spectra, the condensation of acid phosphate groups was demonstrated

In recent years an increased interest in inorganic ion exchangers has appeared The disadvantages of present types of organic ion exchangers as for example the loss of mechanical and ion exchanging properties at higher temperatures, radiation instability at higher levels of ionizing radiation and chemical destruction in strong oxidizing agents were the reason for the development of inorganic ion exchangers Especially useful are the salts of polybasic acids (phosphoric acid, tungstic acid etc) with polyvalent cations (Fe, Bi, Ti, Zr, Th etc), which form polymer hydroxides Due to the selective sorption properties, chemical stability in acids, radiation, mechanical and thermal stability and relatively high exchanging capacity, zirconyl phosphate became the main object of interest

The application of zirconyl phosphate (denoted as ZrP) as a selective sorbent was known as early in the year 1943,(1,2) and a number of fundamental papers(3-10) were published after 1956 Considerable attention was given to the study of the sorption of several elements on ZrP in static as well as dynamic conditions and to the study of the separation of alkaline elements, especially that of cesium (4,6,8,11-19)

---

(1) E R Russell A W Adamson J Schubert and G E Boyd, U S A E C Report CN-508 (1943)

(2) R H Beaton, V R Cooper, B A Fries, T J Chapelle, J Scheft, R A Stoughton and F H Turk, U S A E C Report CN-633 (1943)

(3) C B Amphlett, L A McDonald, J M Redman, *Chem and Industr* 1315 (1956)

(4) K A Kraus and H O Phillips, *J Amer Chem Soc* **78**, 694 (1956)

(5) Anon, *Chem Engng News* **34**, 4760 (1956)

(6) C B Amphlett, *Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva*, Vol 28, p 17 United Nations (1958)

(7) C B Amphlett, L A McDonald and M J Redman *J Inorg Nucl Chem* **6**, 220 (1958)

(8) I J Gal and O S Gal *Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva* 1958 Vol 28 p 24 United Nations (1958)

(9) C B Amphlett *Chem and Industr* 292 (1959)

(10) G H Nancollas and R Paterson, *J Inorg Nucl Chem* **22**, 259 (1961)

(11) C B Amphlett, L A McDonald, J S Burgess and J C Maynard *J Inorg Nucl Chem* **10**, 69 (1959)

(12) T V Healy and B L Davies AERE-M/451 (1959)

Reports of a very advantageous separation processes for the separation of plutonium from fission products on ZrP(1 2,20), on zirconium pyrophosphate(21) and zirconium phosphosilicate(22 23) have been published The separation of two to four valent elements on a paper impregnated by ZrP was described recently (24 25)

Data concerning the structure of the molecule of ZrP and the exchange mechanism are very rare and yield only qualitative conclusions (17 26 28) BURDESE *et al* (29) mentioned in their paper crystalline structures of dehydrated zirconium phosphates The papers of STEGER *et al* (30) and HAIDER(31) deal with the infrared absorption spectrum of a cubic ZrP_2O_7

Due to the fact that only a few authors have described the analysis of ZrP(10 32) in more detail the present work gives an ion exchange method for the separation of zirconium from phosphate anion in ZrP The composition of prepared samples was compared with the results published by BAETSLE *et al* (27) The changes occurring on heating ZrP to various temperatures were observed by measuring the infrared spectra of various types of ZrP From the infra-red spectra obtained and from sorption characteristics for different cations the structural changes, which occurred during the heating of sorbent were explained Systematic comparison of sorption changes for a number of one to four valent cations on ZrP heated to various temperatures is discussed along with the results of ALBERTI *et al* (7) and qualitative conclusions are deduced for the sorption mechanism

EXPERIMENTAL

ZrP sample preparation

Two hundred and forty grammes of $ZrOCl_2 \cdot 8H_2O$ were dissolved in 550 ml of distilled water and precipitated by mixing with 550 ml of $H_3PO_4(Na_3PO_4)$, at a concentration corresponding to the desired ratio of P/Zr at 60 C The precipitate was washed by water until negative reactions were obtained for zirconium and phosphates in the supernatant liquid, dried at 40 C and sieved to 125-135 mesh Samples of ZrP precipitated from 6 N HCl were prepared according to BAETSLE (27)

(13) E M LARSEN and D R VISSERS, *J Phys Chem* **64**, 1732 (1960)

(14) E MERZ, *Z Elektrochem* **63**, 288 (1959)

(15) L BAETSLE and D HUYS, *J Inorg Nucl Chem* **21**, 133 (1961)

(16) K A KRAUS, H O PHILLIPS, T A CARLSON and J S JOHNSON *Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy Geneva*, Vol 28 p 3 United Nations (1958)

(17) G ALBERTI and A CONTE, *J Chromatography* **5**, 244 (1961)

(18) J PROSPERT and T KIKINDAI, *C R Acad Sci Paris* **254**, 860 (1962)

(19) V S ZLOBIN, *Radiokhimija* **4**, 54 (1962)

(20) E R RUSSELL, A W ADAMSON, J SCHUBERT and G E BOYD, US Pat 2 859 093 (1958)

(21) R W STOUGHTON, US Pat 2 970 035 (1961)

(22) Brit Pat 852 501 (1960)

(23) D NAUMANN *Zeit Chem* **1**, 247 (1961)

(24) G ALBERTI and G GRASSINI, *J Chromatography* **4**, 83 (1960)

(25) J M PEIXOTO CABRAL, *J Chromatography* **4**, 86 (1960)

(26) F H WALTON, *Annual Review of Physical Chemistry* **10**, 125 (1959)

(27) L BAETSLE and J PELSMAEKERS, *J Inorg Nucl Chem* **21**, 124 (1961)

(28) J BRIL, *Bull Soc Chim France* 1140 (1960)

(29) A BURDESE and M L BORLERA, *Atti de la Accademia delle Scienze di Torino* **94**, 1 (1959)

(30) F STEGER and G LENKROTH, *Z Anorg Chem* **303**, 169 (1960)

(31) S Z HAIDER, *Anal Chim Acta* **24**, 250 (1961)

(32) P HURST, Doctoral Thesis, University of Wisconsin (1956)

Titration curves

Titration curves of prepared samples of ZrP were determined in a usual way.(13) 0.5 g of ZrP was equilibrated with 75 ml of solution containing sodium chloride and sodium hydroxide at the total concentration of sodium ions of 0.1 N. After reaching equilibrium (seven days) the pH of the aqueous phase was measured.

Equilibrium experiments

Fifty mg of sorbent was always weighed into 25 ml polythene bottles and 5 ml of the solution of the desired cation was added. All solutions were 0.1 N in nitric acid and the initial cation concentration was in the first set of experiments 1.0 × 10^{-5} N, in the second set of experiments 5.3 × 10^{-4} N. The mixture was shaken for three days at room temperature (20°C) and then centrifuged and the equilibrium concentration of the cation in question in the aqueous phase was measured.

Distribution coefficients were calculated as [(meq g^{-1})/(meq ml^{-1})]. For the sorbents heated to 260°C and 1000°C the distribution coefficients were calculated after correcting for the weight loss during heating.

The stock solution of Pu$^{(IV)}$ for equilibrium experiments was prepared by fuming plutonium nitrate twice with concentrated H_2SO_4 and then stabilized by 0.04 N $NaNO_2$.

Analytical methods

The analysis of ZrP. The contents of zirconium and phosphate in the prepared samples of ZrP were determined either directly by a gravimetric method, or gravimetrically after separation of zirconium from phosphate anion on the anion exchanger.

For the gravimetric determination of zirconium 0.2 g of ZrP was dissolved in 20 ml of a saturated solution of oxalic acid and after dilution by distilled water to 150–200 ml, zirconium was determined using cupferron.(14) The presence of oxalic acid does not influence the completeness of the precipitation. The average error in the determination was ±0.3 per cent. After decomposition of ZrP by oxalic acid it is not possible to determine phosphorus either by the phospho-molybdate method or by precipitation of magnesium ammonium phosphate. Also repeated alkaline melting of ZrP with sodium carbonate and potassium pyrosulphate gave low results by 5.5 per cent in the average. Therefore the following procedure was chosen: 0.1–0.15 g of ZrP was dissolved in a Pt crucible by warming with 1–2 ml of 40 per cent hydrofluoric acid and after dilution to 100 ml by distilled water, phosphate was precipitated by molybdate.(15) Due to the fact that the fluoride anions present could not be masked by boric acid, because its presence causes precipitation of ZrP, the precipitation was carried out by lowering the concentration of fluoride anions to a minimum. After the first precipitation the precipitate was left standing for 18 hr and the precipitation was repeated three times. The factor (0.01651) was verified by titration.(15) The average deviation of a determination was ±1.0 per cent.

For the separation of zirconium from phosphate anion 0.1–0.2 g of ZrP was dissolved in 30 ml of saturated oxalic acid and the solution was passed through the column filled with anion exchanger (Dowex-1), at the flow rate 0.93 ml cm^{-2} min^{-1}. Dowex-1 in the hydroxyl form was transformed into the oxalate form by adding a saturated solution of oxalic acid and washing with distilled water. After sorbing the dissolved ZrP the column was washed with a saturated solution of oxalic acid (washing with water may cause low results because of the precipitation of ZrP in the column) and zirconium was eluted by 150–200 ml of 4–6 N HCl at a flow rate of 0.93 ml cm^{-2} min^{-1}. The solution was acidified with 40 ml of sulphuric acid (1:1) and zirconium determined by cupferron(14) precipitation. Phosphorus was determined in the solution after washing with oxalic acid. The solution was evaporated to dryness 2–3 times with nitric acid to decompose the oxalate ions present. The dry residue was dissolved in 10 ml of concentrated nitric acid and after adjusting the volume to 100–150 ml phosphorus was determined as phosphomolybdate.(15) After repeated separation processes the colour of the ion exchanger darkens without the separating qualities being affected.

N. E. Topp and K. W. Pepper, *J. Chem. Soc.* 3299 (1949).

A. Jílek and J. Koťa, *Vážková analysa a elektroanalysa* Vol. 2, p. 611. Technicko-vedecke nakladatelstvi, Prague (1951).

W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis* p. 560. J. Wiley, New York (1948).

The chloride content of ZrP was determined in the following way. 0.4 g of ZrP was dissolved in 10 ml of ammonium fluoride solution (10 g/100 ml) by heating. After dilution to 150 ml 1.5 ml of 0.1 N HCl was added and then the solution was titrated potentiometrically with 0.01 N AgNO$_3$.(36) Under these conditions the fluoride anions do not influence the determination. It was necessary to add 0.1 N HCl because of the small chloride content in the ZrP samples.

The analysis of exchangeable cations. Sodium and potassium were determined by the flame photometry method; cesium was determined by ^{137}Cs labelling; strontium was determined in concentrations 10^{-2} N by titration with EDTA (disodium salt) with methylthymol blue(37) as indicator, at lower concentrations by ^{90}Sr labelling; uranium was determined at concentrations 10^{-2} N spectrophotometrically by the peroxide method at 350 mμ,(38) at lower concentrations by Arsenazo III method at 650 mμ;(39) zirconium was determined spectrophotometrically in the sorption experiments by xylenol orange at 535 mμ,(40) at concentrations 10^{-3} N by Arsenazo III at 615 mμ; cerium(III) was determined at concentrations 10^{-2} N by titration with EDTA (disodium salt) with brompyrogallol red(41) as indicator, at lower concentrations by ^{144}Ce labelling. ^{144}Ce was used in the trivalent form prepared according to ref.(42) Iron(III) was determined at concentrations 10^{-2} N by iodometric titration,(43) at lower concentrations spectrophotometrically by Arsenazo III at 615 mμ; bismuth(III) was determined by titration with EDTA (disodium salt) with pyrokatechin violet as indicator;(44) nitrosylruthenium(III) was determined polarographically in 0.5 N HClO$_4$.(45) Thorium(IV) was determined at concentrations 10^{-2} N by titration with EDTA (disodium salt) with pyrocatechin violet as indicator,(46) at lower concentrations spectrophotometrically by Arsenazo III at 665 mμ.(39) Plutonium(IV) was determined at concentrations 10^{-2} N by titration with EDTA (disodium salt) with Arsenazo I as indicator,(47) at lower concentrations radiometrically by measuring the α-radiation of ^{239}Pu.

Measurements of infra-red absorption spectra

Samples for measurements of infra-red spectra of ZrP were prepared by the standard KBr-pellet technique.(48) One to two mg of the substance was ground with 1 g of potassium bromide, 300 mg of the mixture was then pressed (15 ton/cm^2) into a pellet. Measurements were carried out in comparison with the KBr blank pellet.

Instruments and reagents used

The pH of the solutions was measured with pH-meter PHM 22 made by Radiometer-Copenhagen. Flame-photometric measurements were carried out on a flame photometer produced by Karl Zeiss in Jena, with Na 59 and K 77 filters. Spectrophotometric measurements were carried out on Universal spectrophotometer made by Karl Zeiss, Jena. Infra-red absorption spectra were measured on infra-red spectrophotometer UR 10, made by Karl Zeiss, Jena. For radiometric measurements of α-emitters the scintillation gauge TJU-ZnS/Ag/(USSR) with decade scaler was used in the usual manner. For the measurements of β–γ-emitters the apparatus SČ-4 (USSR) was used.

All reagents used were of analytical grade.

(36) O. TOMIČEK, *Odměrná analysa*. Československá společnost chemická, p. 294. Prague (1949).

(37) J. KORBL and R. PŘIBYL, *Chem. listy* **51**, 1061 (1957).

(38) C. J. RODDEN, *Analytical Chemistry of the Manhattan Project*, p. 94. McGraw-Hill, New York (1950).

(39) S. V. SAVVIN, *Dokl. Akad. Nauk USSR* **127**, 1231 (1959).

(40) K. L. CHENG, *Talanta* **2**, 61 (1959).

(41) A. JENIČKOVA, V. SUK and M. MALAT, *Collection Czechosl. Chem. Communs* **21**, 1257 (1956).

(42) V. V. FOMIN, P. E. KARTUŠOVA and T. J. RUDĚNKO, *Zh. neorg. Khim.* **3**, 2117 (1958).

(43) A. JÍLEK, *Odměrná analysa*, Vol. 2, p. 291, Technicko-vědecke vydavatelství, Prague (1951).

(44) M. MALAT, V. SUK and O. RYBA, *Collection Czechoslov. Chem. Communs* **19**, 258 (1954).

(45) D. M. WAGNEROVA, *Symposium on Co-ordination Compounds*. Prague (1960).

(46) V. SUK, M. MALAT and O. RYBA, *Collection Czechoslov. Chem. Communs* **19**, 679 (1954).

(47) P. N. PALEJ and ČŽAN VEŇ-CIN, *Zhur. Anal. khim.* **15**, 598 (1960).

(48) M. M. STIMSON, *J. Amer. Chem. Soc.* **74**, 1805 (1952).

RESULTS AND DISCUSSION

Separation of zirconium from phosphate anion on an anion exchanger

For the complete separation of phosphate anion from zirconium the separation on anion exchangers is a very appropriate method. Korkisch *et al.*(49) describe the separation of zirconium from phosphate anion on strongly basic anion exchangers from 0.1 N H_2SO_4 and NaF (0.1 g/ml). Due to the fact that the break-through capacity in this method is relatively low, an ion exchange separation from oxalate medium was developed, where the break-through capacity is in comparable conditions 17 times greater so that it is possible to determine single components after separation by gravimetric methods. The separation of zirconium from phosphate anions is quantitative and the oxalate complex of zirconium is fixed very firmly on the exchanger, so that it is possible to carry out the sorption at a relatively faster flow-rate and for its complete elution 4–6 N HCl is found to be the most appropriate. The mixture of 6 N HCl and 0.5 N NH_4F does not influence substantially the desorption rate.

The results of zirconium and phosphorus analysis after the separation has been carried out are indicated in Table 1. The results verify the completeness of the separation and practically total desorption of zirconium, their deviations are caused by errors in the gravimetric analysis.

TABLE 1. RESULTS OF SOME DETERMINATIONS OF ZIRCONIUM AND PHOSPHORUS AFTER SEPARATION ON ANION EXCHANGER

Zirconium		Phosphorus	
Sorbed (mg)	Found (mg)	Sorbed (mg)	Found (mg)
44.2	44.6	22.2	21.2
44.4	44.0	22.3	23.6
36.3	36.3	22.3	22.7
35.8	34.7	22.5	22.6
35.5	36.7	22.4	21.8
35.4	36.0	22.2	22.8
34.8	34.7	21.9	21.8

Dowex 1-X 8 ($C_2O_4^{2-}$), 20–50 mesh, column dimensions 15 cm 0.97 cm²

P/Zr ratios in various prepared ZrP samples

The conditions under which the various types of ZrP were prepared had a substantial influence on the resulting P/Zr ratio in the precipitate. In Table 2 the P/Zr ratios before the precipitation under different precipitation conditions and P/Zr ratios in the washed precipitate are listed. The results of ZrP precipitation from H_3PO_4–6 N HCl and $H_3PO_4(NaH_2PO_4)$ 0.1 N HCl are taken from the works of Baetsle *et al.*(27) and Larsen *et al.*(13) for comparison. It is evident from Table 2 that the precipitates of ZrP are formed with relatively small phosphate contents during precipitation by a tertiary sodium phosphate, where even a higher phosphate excess with regard to zirconium in the initial mixture does not substantially increase the P/Zr ratio in the precipitate. This is because of the hydrolysis of ZrP in an alkaline medium.⁽¹³⁾ During precipitation from H_3PO_4–6 N HCl (even at a ratio of P/Zr = 3 in the initial mixture) the P/Zr ratio in the precipitate does not exceed the value of 1.66.⁽²⁷⁾ BAETSLÉ *et al.*⁽²⁷⁾ explain this fact by steric hindrance in the ZrP chain. On the other hand we have prepared ZrP samples with the ratio of P/Zr = 1.86 by precipitation with H_3PO_4, NANCOLLAS *et al.*⁽¹⁰⁾ prepared a sample with the ratio of 1.86, LARSEN *et al.*⁽¹³⁾ prepared by the precipitation in H_3PO_4–0.1 N HCl also a sample with a higher ratio (1.72). Digesting our ZrP sample having the ratio of P/Zr = 1.86 with 20 per cent phosphoric acid at 60°C and washing with considerable volumes of water until a negative reaction for phosphates in supernatant solution was obtained, we found in the first sample the ratio of P/Zr = 2.00, in the second 2.02. This is similar to a result of MERZ,⁽¹⁴⁾ who obtained samples with higher content of phosphorus by digestion with phosphoric acid.

---

(49) J. Korkisch and A. Farag, *Z. Analyt. Chem.* **166**, 170 (1959).

TABLE 2.—P/Zr RATIO IN INITIAL SOLUTION AND IN PRECIPITATE

Precipitation medium	P/Zr in initial solution	P/Zr in precipitate
6 N HCl	3.0	1.47
H_3PO_4	3.0	1.68⁽²⁷⁾
	2.0	1.66⁽²⁷⁾
	1.5	1.50⁽²⁷⁾
	0.94	0.94⁽²⁷⁾
0.1 N HCl⁽¹³⁾	4.0	1.72
H_3PO_4	1.5	1.29
(NaH_2PO_4)		
H_3PO_4	2.5	1.86
	1.35	1.41
	0.5	0.88
0.1 N HCl	1.5	0.69
Na_3PO_4		

In Table 3 the changes of the P/Zr ratio after fivefold digestion of the ZrP samples with 4 N HCl are given. From the results given it is obvious that the digestion with 4 N HCl reduces the P/Zr ratio of the samples with higher phosphate contents. On the other hand, the digestion of the sample with a low P/Zr ratio causes its increase (from 0.88 to 1.07). This may be due to solution of zirconium. The composition of ZrP with the P/Zr ratio of 1.41 does not change during this digestion. The decrease of P/Zr ratio by digestion with 4 N HCl is in accordance with the fact, that ZrP samples with lower P/Zr ratio are obtained by precipitation from 6 N HCl than by precipitation without added HCl. This may be explained by chloride ion incorporation into ZrP. It may be seen from the Table 3 that the samples precipitated from 6 N HCl or digested with 4 N HCl, washed with acetone until a negative reaction for chloride ions occurred,

TABLE 3 —INFLUENCE OF HCl ON THE COMPOSITION OF ZrP

Precipitation medium	P/Zr in precititate	P/Zr after digestion with 4 N HCl	Chloride content (%) after precipitation (washed with acetone)	Chloride content (%) after digestion with 4 N HCl (washed with acetone)
6 N HCl H_3PO_4	1 47	-	2 86	—
H_3PO_4	2 02*	1 93	-	0 37
	1 86	1 79		
	1 41	1 42		-
	0 88	1 07		

* This sample was prepared by digestion of a ZrP sample (P/Zr 1 86) with 20% H_3PO_4 at 60°C

contain a remarkable amount of chloride The Cl content is reduced to a negligible value (from 2 86 to 0 03 per cent and from 0 37 to 0 01 per cent) by further washing with water If the samples have been washed with water only, the chloride ions were not found

Then we may conclude that a lower P/Zr ratio obtained by precipitation from hydrochloric acid is caused by chloride ions incorporated into the exchanger These chloride ions are removed by washing with water and replaced by OH groups

Titration curves

In order to characterize more completely the ZrP samples prepared by precipitation with phosphoric acid, their titration curves are presented in Fig 1 and compared with those of AMPHLETT *et al*[7] and BAETSLÉ *et al*[27] The titration curves have a less steep slope and do not show the inflexion points in comparison with those of other authors[7,27]

Distribution coefficients of 1-4 *valent cations*

In Table 4 the distribution coefficients of some 1 4 valent cations (on ZrP with ratios of P/Zr 1 0 and 1 87) for sorbents dried at 40°, 260° and 1000 C are shown All the values given are valid for an equilibrium concentration of nitric acid in the aqueous phase of 0 1 N and a total cation concentration of 10^{-3} N

From Table 4 it is evident that the distribution coefficients (K_d) of practically all the cations in question are lower for the ion exchanger dried at 260°C than for the ion exchanger dried at 40°C It is possible to explain this fact by the condensation of acid

TABLE 4 —DISTRIBUTION COEFFICIENTS FOR SOME 1 4 VALENT CATIONS

P/Zr	Drying temperature (°C)	K_d											
		Na^+	K^+	Cs^+	Sr^{2+}	ZrO^{2+}	UO_2^{2+}	Ce^{3+}	Fe^{3+}	Bi^{3+}	$RuNO^{3+}$	Th^{4+}	Pu^{4+}
1 0	40		9 5	26 3		361	1 0	5 1	37 9	700	5 5	130	1290
	260	—	8 0	14 5	—	252		2 6	34 2	219		75	359
	1000	-	9 6	10 0		2 5		1 6	1 0	1 0		1 0	16 0
	40	10 0	19 5	349	1 0	1400	597	43 5	6570	8000	5 5	2760	5550
	260	8 8	21 0	126	1 0	450	176	3 9	315	1000	-	504	684
	1000	—	3 7	4 3	—	24 0		2 7	3 7	8 7		5 5	52 4

For cations where hydrolysis may be expected under the given conditions an indication of the unhydrolysed form is

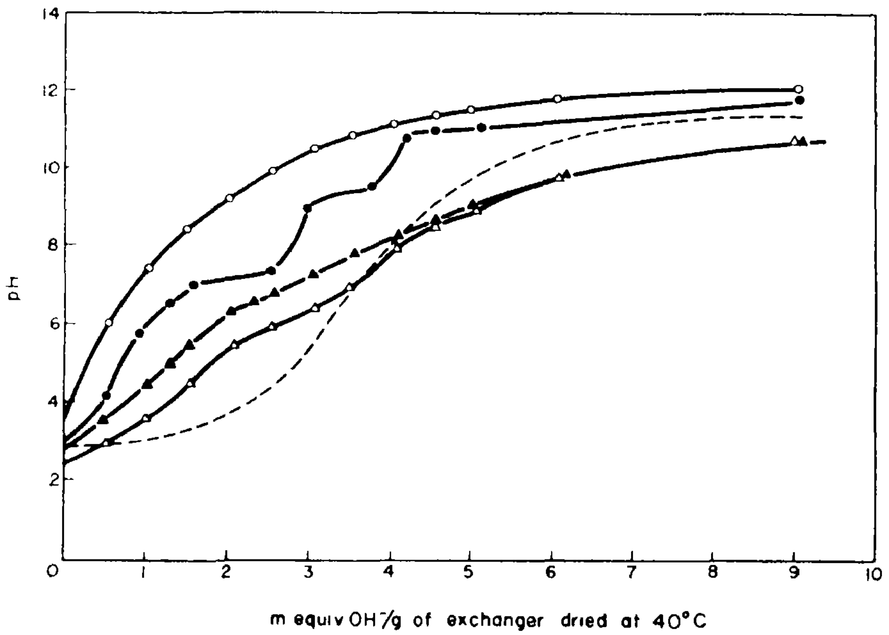


FIG. 1. Titration curves of ZrP with different P/Zr ratios.
P/Zr 1.79 precipitated with H_3PO_4
▲—P/Zr 1.42, precipitated with H_3PO_4
P/Zr 1.07, precipitated with H_3PO_4
●- P/Zr in initial solution 1.44, precipitated with H_3PO_4 from 1 N HNO_3, AMPHLETT *et al.*(7)
--- P/Zr 1.25 precipitated with H_3PO_4 from 6 N HCl, BAETSLÉ *et al.*(27)

phosphate groups of ZrP to P–O–P groups during heating the ion exchanger, as may be seen from infra-red spectra measurements. The concentration of exchangeable hydrogen ions in the ion exchanger phase and therefore K_d of a given cation are decreased in this way. This finding does not agree with the measurements of ALBERTI *et al.*(24), that the K_d values of the alkaline cations (K^+, Rb^+, Cs^+) and Tl^+ increase at 260°C. The cations Na^+, K^+, Cs^+, which were investigated by us, show a distinguishable decrease of K_d. All K_d values for the ion exchanger with a higher phosphate content (i.e. with a higher content of the functional group) are higher than those of ion exchangers with the lower phosphate content. It is interesting to find the sorption, in some cases with high K_d values (Pu^{4+}), on ion exchangers heated to 1000°C, where no ion exchange mechanism any more may be considered. This statement is confirmed also by the work of STOUGHTON,(21) who studied plutonium sorption on zirconium pyrophosphate. Heated samples of ZrP contain zirconium pyrophosphate (ZrP_2O_7) or a mixture of structures of ZrP_2O_7, $(ZrO)_2P_2O_7$ and ZrO_2 (see below). We assume a coordination of the polyvalent cations (Pu^{4+}, Th^{4+}, Fe^{3+}, Bi^{3+}) and ZrO^{2+} on oxygen atoms of the P_2O_7 group. It is difficult to explain the sorption of K^+ and Cs^+ on ZrP heated on 1000°C. It is impossible to assume the sorption (from 0.1 N HNO_3) on ZrO_2 present in the sorbent. The assumption of sorption onto reconstituted acid phosphate groups formed by hydrolysis on immersion in water is not in accord with the infra-red spectra measurements. No change was found in the spectra of ZrP heated on 1000°C by digestion with water or 0.1 N HNO_3. Later no sorption of K^+ and Cs^+ was found on pure ZrP_2O_7, prepared according to STEGER *et al.*(30)

Values of K_d of individual alkaline cations follow the series $Cs^+ > K^+ > Na^+$, which is usual for cation exchangers. Their mutual separation factors are higher for an ion exchanger with a higher phosphate content. From Table 4 it may be seen that divalent cations (with the exception of ZrO^{2+}) have very low distribution coefficients in accordance with the fact that divalent cations are very weakly retained on ZrP(6,8) in a weakly acid medium. The highest K_d values were found for Pu^{4+}, Th^{4+}, Bi^{3+}, Fe^{3+} and ZrO^{2+}, that is cations whose phosphates are very slightly soluble and which have a great affinity for the phosphate group. In addition, the possibility of forming a coordination bond with an oxygen atom of the phosphate group may occur. Very small distribution coefficients found for $RuNO^{3+}$ are in accordance with experiments in dynamical conditions, when $RuNO^{3+}$ at an acidity about 0.1 N is hardly retained at all.

TABLE 5. EQUILIBRIUM UPTAKE OF SOME 1–4 VALENT CATIONS ON ZrP

Drying temperature (°C)	Uptake in meq/g				
	Na^+	K^+	Cs^+	Sr^{2+}	ZrO^{2+}
40	0.20	0.54	1.03		0.34
260	0.17	0.41	0.27	–	
1000					–

Drying temperature (°C)	Uptake in meq/g					
	UO_2^{2+}	Ce^{3+}	Fe^{3+}	$RuNO^{3+}$	Th^{4+}	Pu^{4+} *
40	0.1	0.7	0.1	—	1.24	1.12
260		0.16	–	– –	0.1	0.89
1000			– –	– –	0.1	0.63

66 mg ZrP (P/Zr = 1.95), 5 ml of 5.3×10^{-2} N solution of cation in 1.0 N HNO_3.

* 0.67 N HNO_3, 8.96×10^{-2} N Pu.

In Table 5 the equilibrium uptake of some cations in meq/g for ion exchanger with the ratio of P/Zr = 1.95 for various drying temperatures are given. The initial concentration of HNO_3 was 0.1 N and the total concentration of cation was 5.3×10^{-2} N. 66 mg of ZrP was equilibrated with 5 ml of the solution.

In Table 5, the relatively high uptake of Pu^{4+} may be seen especially when the ion exchanger is heated to 1000°C. In this case the uptake of practically all other cations is immeasurably small.

Infra-red absorption spectra of ZrP *at various drying temperatures*

In Fig. 2 infra-red absorption spectra of ZrP samples with ratios of P/Zr = 1.0, 1.7 and 1.95 heated during 24 hr to 1000°C are shown. The spectra of heated samples having the ratios of 1.7 and 1.95 are similar to the spectrum of cubic zirconium pyrophosphate (ZrP_2O_7) measured by STEGER *et al.*(30) and HAIDER.(31) The comparison of the absorption maxima found with those of STEGER *et al.*(30) and HAIDER(31) is given in Table 6. Thus by heating ZrP with P/Zr ratios of 1.7 and 1.95 zirconium pyrophosphate is formed; for a sample with the ratio of P/Zr = 1.7 a certain amount of ZrO_2 must be considered also. The ZrP spectrum of a sample with P/Zr ratio of 1.0 heated to 1000°C is different from the foregoing. Its absorption maxima are given in Table 6. This spectrum may be ascribed to zirconyl pyrophosphate $(ZrO)_2P_2O_7$. This is confirmed also by the fact, that by heating a mixture of ZrO_2 and ZrP_2O_7 at 1200°C $(ZrO)_2P_2O_7$ is formed.(29) The infra-red absorption spectrum of the mixture of ZrO_2 and ZrP_2O_7 heated to 1250°C, measured by us is practically identical with the spectrum shown in Table 6. Of course it is not possible to exclude the presence of ZrP_2O_7 and ZrO_2 due to a lower heating temperature (1000°C instead of 1250°C).

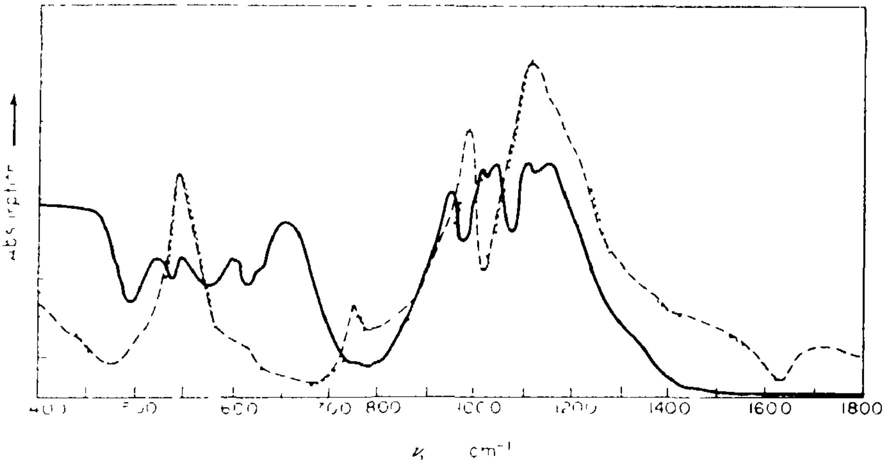


FIG. 2. Infra-red absorption spectra of ZrP with various P/Zr ratios after heating to 1000°C.
P/Zr 1.0
---- P/Zr 1.7
P/Zr 1.95

The knowledge of the infra-red spectrum of zirconium pyrophosphate (ZrP_2O_7) as well as the fact that the absorption maximum within 958–983 cm^{-1} is ascribed to the valency vibration of P–O–P,(30) enabled us to investigate the condensation course of acid phosphate groups of ZrP during its heating. In Figs. 3 and 4 are the infra-red spectra of the ZrP sample with the P/Zr ratio of 1.95 heated to 260°C, 450°C, 700°C, 800°C, 850°C and 1000°C. The gradual change of the ZrP structure to the ZrP_2O_7 structure with increasing temperature is obvious. The results given in Figs. 3 and 4 confirm the assumption expressed by AMPHLETT *et al.*(7) and ALBERTI *et al.*(17) concerning condensation of acid phosphate groups to P–O–P groups at heating ZrP. By comparing the spectrum of ZrP heated to 260°C with the spectra of prepared mixtures of ZrP and ZrP_2O_7 it may be deduced that about 20 per cent of phosphate groups are condensed at 260° and about 60 per cent at 450°C. Therefore it is not possible to ascribe the weight loss after heating to 100–400°C only to the loss of co-ordinated water, as assumed by BAETSLÉ *et al.*,(27) but also to the loss of water in consequence of the condensation of acid phosphate groups to P–O–P groups. According to our measurements this condensation begins as early as 250°C and probably at a still lower temperature, because we could determine, by the method of infra-red spectroscopy,

TABLE 6.—INFRA-RED ABSORPTION MAXIMA OF ZrP HEATED TO 1000°C WITH P/Zr RATIOS OF 1.0 AND 1.95

cm^{-1}			
P/Zr 1.0	P/Zr 1.95	ZrP_2O_7 SIEGER *et al.*(30)	ZrP_2O_7 HAIDER(31)
		500	
520–530 *mb*			
550 *m*	549 *s*	548	
602 *m*			
624 *w*			
645–665 *sb*			
			720 *s*
	745 *m*	750	740 *w*
947 *s*			
	981 *vs*	958–983	975 *vs*
1019 *s*			
1048 *s*			
1108 *s*	1112 *vsb*	1058–1125	1075–1125 *sb*
1146 *s*			1155 *w*

w—weak, *m*—middle, *s*—strong, *vs*—very strong, *b*—broad

TABLE 7.—PER CENT WEIGHT LOSS OF ZrP (P/Zr = 1.95) AFTER HEATING TO VARIOUS TEMPERATURES

Temperature (°C)	Weight loss (%)
100	6.4
260	12.4
450	15.2
700	17.9
800	18.8
850	19.2
1000	19.2

the P–O–P groups in the presence of PO_4 groups only at a greater content than 10 per cent of P–O–P groups.

By condensation of acid phosphate groups it is possible to explain also the lower values of distribution coefficients of practically all cations studied on ZrP heated to 260°C compared to the ZrP dried at 40°C (Table 4). Condensation decreases the concentration of exchangeable hydrogen ions in the sorbent phase and therefore causes a lower sorption of cations.

We can see from Fig. 4 that the infra-red spectrum of the sample heated to 850°C is similar to that of ZrP_2O_7, from which it appears that the condensation is at the end at 850°C. This agrees with the results of the weight loss measurements given in Table 7.

If the ZrP is converted to the Na^+ or K^+ form by treatment with a solution of 1 N $Na(K)NO_3$ (pH 7–8) and heated to 1000°C its infra-red spectrum is completely

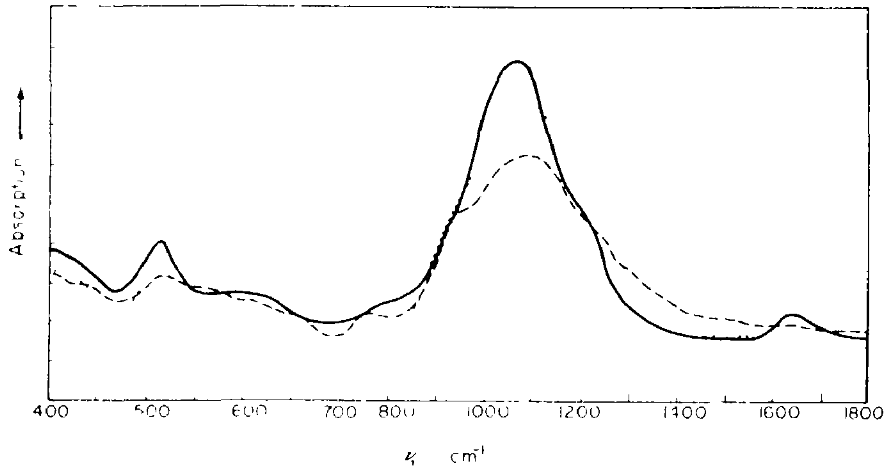


FIG. 3 — Infra-red absorption spectra of ZrP with P/Zr ratio of 1.95 dried at 40 °C, 260 °C and 450 °C

40 °C
-260 °C
- - - - 450 °C

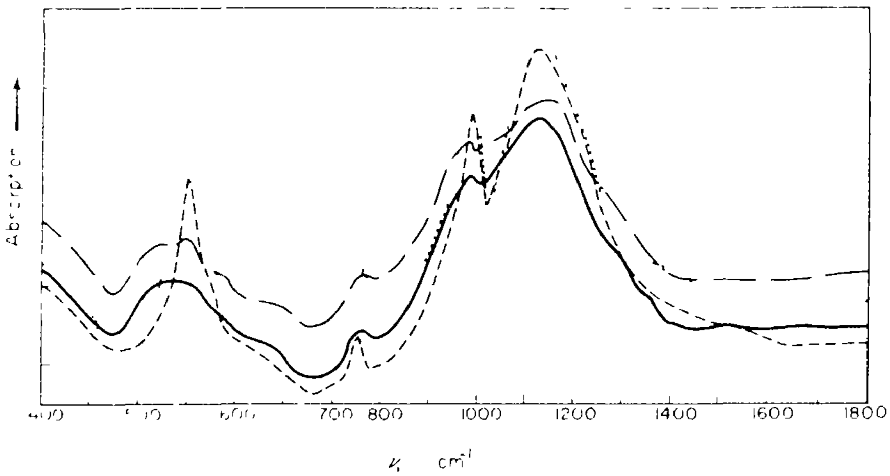


FIG. 4 — Infra-red absorption spectra of ZrP with P/Zr ratio of 1.95 dried at 700 °C, 800 °C, 850 °C and 1000 °C

—— 700 °C - - - -—850 °C
—800 °C -1000 °C

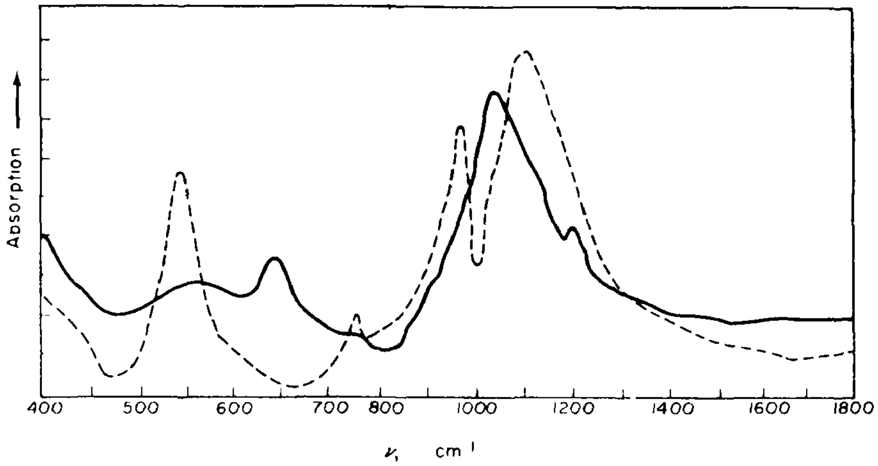


Fig 5—Infra-red absorption spectrum of ZrP with P/Zr ratio of 1 95, in H and K form after heating to 1000 C

- - - - H form
—— K form

different from that of ZrP_2O_7 A comparison is given in Fig 5 From the figure it is evident that the characteristic frequency of P–O–P at 981 cm^{-1} is strongly suppressed in the spectrum of heated ZrP in K$^+$ form This shows that sodium or potassium ions hinder the condensation of acid phosphate groups on heating the ion exchanger and that these ions substituted acid hydrogen ions of the phosphate group by a mechanism of ion exchange

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 711 to 718. Pergamon Press Ltd. Printed in Northern Ireland

THE PROCESSING OF PLUTONIUM BY ION EXCHANGE—I

THE CONCENTRATION DEPENDENCE OF DISTRIBUTION COEFFICIENTS ON DOWEX 1X4 FROM 7 M NITRIC ACID*

D. B. JAMES
Los Alamos Scientific Laboratory, University of California Los Alamos, New Mexico

(*Received* 18 *June* 1962, *in revised form* 2 *November* 1962)

Abstract—An expression was derived and experimentally confirmed for the change in the volume distribution coefficient for plutonium (IV) on Dowex 1X4 from 7 M nitric acid with varying concentrations of plutonium (IV) in the aqueous phase. A few experiments with other sorbable species indicate the equations may be applicable to other systems. These calculations require one measurement of the volume distribution coefficient at a trace level of resin loading. These trace level coefficients were determined for many elements.

THE sorption of plutonium (IV) by anion-exchange resins from nitric acid solutions was demonstrated by DURHAM and MILLS.(1)

RYAN and WHEELWRIGHT(2) studied most of the parameters concerned with the sorption and desorption of plutonium (IV) on several types of anion-exchange resins from strong nitrate solutions. Nitrate salt solutions give higher equilibrium sorption but lower sorption rates. From nitric acid the equilibrium sorption is somewhat lower, but more favourable kinetics yield better process behaviour in anion-exchange columns. The equilibrium sorption passes through a maximum between 7.0 and 7.5 M nitric acid. These results lead to the choice of 7 M nitric acid as a satisfactory solvent for the purification of plutonium by anion exchange.

Plutonium (IV) is also sorbed by anion-exchange resin from sulphate or chloride systems.(3) However, many other metallic species are sorbed from these solvents. The success of the nitrate system is largely due to its high specificity. Only a few elements are sorbed to any significant degree by nitrate-form anion-exchange resin from 7 M nitric acid. This degree of sorption has been investigated by several workers.(2–12) However, these studies were made on various types of resins and often without regard to the degree of resin loading.

---

* Work done under the auspices of the U.S. Atomic Energy Commission.

(1) R. W. DURHAM and R. MILLS, *AECL Pub.* CEI 62 (1953).
(2) J. L. RYAN and E. L. WHEELWRIGHT, Paper at 113*th Nat. Meeting Amer. Chem. Soc.* San Francisco (1958).
(3) I. R. BURNEY, N. F. BALLOU, J. PASCUAL and S. FOTI. AEC Pub. NRDL-TR-228 (1958).
(4) R. F. BUCHANAN and J. P. FARIS, *Conference on the Use Radioisotopes Phys. Sci. and Chem.*, paper RICC/173, Copenhagen, Denmark (1960).
(5) F. NELSON and K. A. KRAUS. *ASTM Special Tech. Pub.* **195**, 27 (1956).
(6) J. DANON, *J. Amer. Chem. Soc.* **78**, 5953 (1956).
(7) F. NELSON and K. A. KRAUS, *J. Amer. Chem. Soc.* **75**, 5916 (1954).
(8) E. H. HUFFMAN, R. L. OSWALT and L. A. WILLIAMS, *J. Inorg. Nucl. Chem.* **3**, 49 (1956).
(9) D. NAUMAN and R. ROSS, *Kernenergie* **3**, 425 (1960).
(10) J. L. RYAN, *J. Phys. Chem.* **64**, 1375 (1960).
(11) J. L. RYAN, *J. Phys. Chem.* **65**, 1099 (1961).
(12) F. ICHIKAWA, S. URUNO and H. IMAI, *Bull. Chem. Soc. Japan* **37**, 962 (1961).

The volume distribution coefficient for a sorbable element, S, is defined by

$$D_v^S = \frac{\text{Amount of S/ml of resin bed}}{\text{Amount of S/ml of solution}} \qquad (1)$$

Only at very low degrees of resin loading say less than one per cent, does this quantity become reasonably constant Therefore these measurements are not strictly applicable except for measurements and applications made at the same fraction of resin loading The purpose of this study was to investigate the manner in which the distribution coefficients for plutonium (IV) and other elements change with their concentration in either phase Then trace-loading measurements could be applied at practical process concentrations

EXPERIMENTAL

Reagents The resin used in these experiments was Dowex $1X4(50\text{-}100)NO_3$ It was converted from the chloride to the nitrate form by a batch-wise cyclic treatment with a 0 3 M ferric nitrate 2 5 M nitric acid solution, a 3 0 M nitric acid solution and water until a silver nitrate test for chloride was negative The equivalent capacity per unit volume for anions of the resin used was determined by converting a measured volume of resin in contact with 7 M nitric acid to the hydroxide form, passing an excess of standard 0 1 M hydrochloric acid over the resin, and back titrating the effluent with standard sodium hydroxide The average of three determinations was 1 16 milliequivalents per millilitre of nitrate-form resin The impurities in the plutonium used were less than 0 01 weight per cent except for 2 6 per cent iron, 0 20 per cent uranium, 0 47 per cent americium and 0 02 per cent aluminium The isotopes used were obtained from Union Carbide Nuclear Co and, except for a very large dilution with 7 M nitric acid, were used as received All other reagents were analytical grade or better

Batch equilibration experiments For species with a relatively high distribution coefficient the batch equilibration method was used A measured volume of resin in 7 M nitric acid was filtered 'dry' with vacuum and then added to a measured volume of 7 M nitric acid solution, containing a known amount of the metallic ion to be investigated This mixture was shaken for at least 50 hr with a wrist-action shaker, and then the concentration of the metal in the aqueous phase was again measured The volume distribution coefficient was calculated according to the formula

$$D_v^S = \frac{\text{(Volume aqueous phase)(Concentration change aqueous phase)}}{\text{(Volume resin phase)(Final concentration aqueous phase)}} \qquad (2)$$

In the case of plutonium (IV) several measurements were made with one system by removing a measured volume of the aqueous phase and adding a measured volume of 7 M nitric acid between equilibrations U(VI), Th(IV) and Au(III) solutions were all analyzed spectrophotometrically, U(VI) using arsenazo reagent, Th(IV) using thoron and Au(III) using rhodamine B The plutonium solutions were analysed by α-counting with a correction for the americium present, determined by γ-counting

Column experiments For species with a relatively low distribution coefficient, the column method of KRAUS and MOORE[13] was used to measure D_v^S A column was constructed of one metre of 5 mm (i d) glass tubing with a porous frit to support the resin bed It can be shown that

$$D_v^S = \frac{V}{dA} - i, \qquad (3)$$

where V is the volume of solution required to move the maximum of a sorbed band a distance d, if the column has a cross sectioned area A and the fractional interstitial void space about the resin beads is i The evaluation of i is discussed later

For coloured species d was measured by visual inspection For colourless species with an available γ- or β-active isotope d was measured by scanning the column with a shielded G-M tube and recording the integrated signal on a moving chart recorder A photograph of this apparatus is shown in Fig 1

---

[13] K A KRAUS and G E MOORE, *J Amer Chem Soc* 75, 1460 (1953)

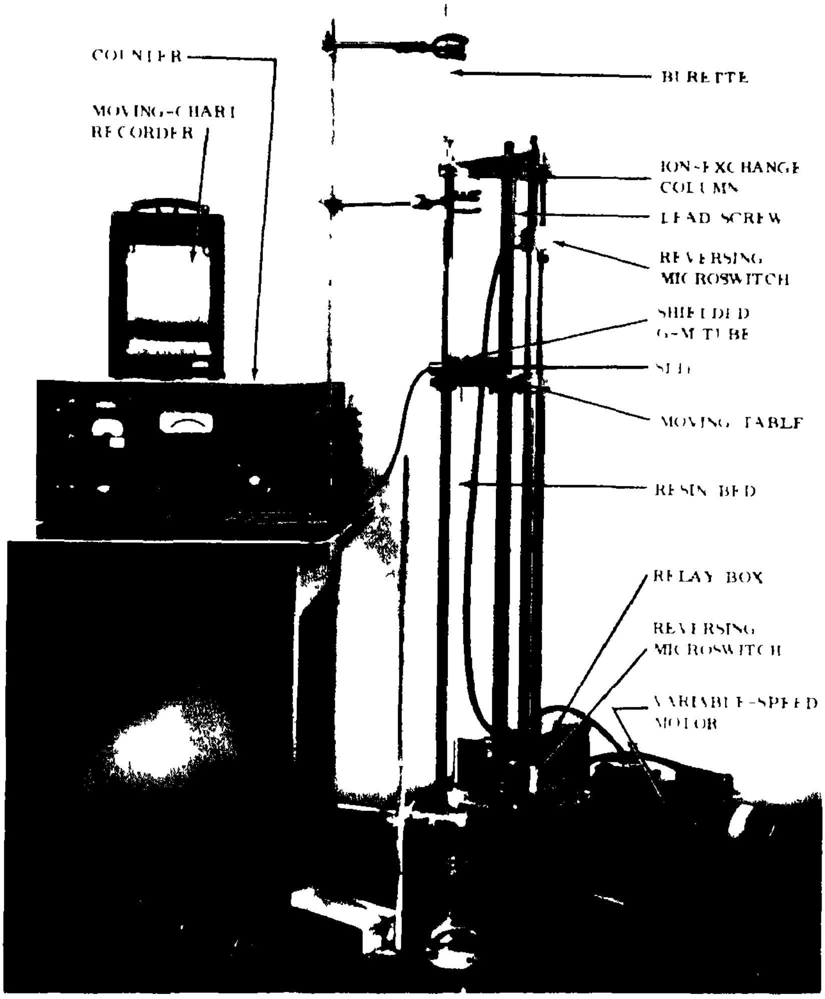


FIG. 1 —Column scanning device

A triangular table held the G-M tube, and it was raised and lowered by a vertical lead screw at its center. The table rode on three vertical legs over a maximum distance of one meter. Microswitches reversed the direction of the variable speed motor, which drove the lead screw, at the top and bottom of the travel. Scanning rates from one to 20 cm/min were available. The chart recorder only moved while the table was lowering. The G-M tube was shielded in a block of lead with a small, variable slit. One hundredth of a millicurie of energy was sufficient for each experiment. The specific tracers used in these experiments were ^{110}Ag, ^{76}As, ^{210}Bi, ^{109}Cd, ^{141}Ce, $^{152-154}$Eu, ^{181}Hf, ^{114}In, ^{59}Fe, ^{140}La, ^{203}Hg, ^{99}Mo, ^{95}Nb, ^{191}Os, ^{32}P, ^{186}Re, ^{153}Sm, ^{124}Sb, ^{46}Sc, ^{75}Se, ^{113}Sn, ^{182}Ta, ^{204}Tl, ^{170}Tm, ^{185}W, ^{90}Y and ^{65}Zn.

For those species which are not sufficiently coloured and have no available γ- or β-active isotope d was measured by chemical analysis of consecutive fractions of the eluate. This method has the disadvantage of requiring many analyses and yielding only one measurement with each experiment. The other column methods allow analysis-free simultaneous measurements of d and V at several stages during the elution. D_1 was then determined by averaging the results of these several measurements.

In all these column experiments the loading solution contained 7 M nitric acid and only enough of the metallic species to load less than one percent of the resin sites in a band of about 1 cm in length at the top of the column. The eluant was always 7 M nitric acid.

RESULTS AND CONCLUSIONS

RYAN$^{(10)}$ has shown that the species of plutonium (IV) that is sorbed by anion-exchange resins from 7 M nitric acid is probably $Pu(NO_3)_6^{2-}$. The exchange reaction would be,

$$Pu(NO_3)_6^{2-} + \overline{2NO_3^-} \rightleftharpoons \overline{Pu(NO_3)_6^{2-}} + 2NO_3^- , \tag{4}$$

where the bar indicates a species associated with resin sites within the resin phase. An equilibrium quotient for this reaction could be written,

$$K_{Pu} = \frac{[\overline{Pu(NO_3)_6^{2-}}][NO_3^-]^2}{[Pu(NO_3)_6^{2-}][\overline{NO_3^-}]^2}, \tag{5}$$

The brackets indicate molar concentrations in the aqueous phase and moles per litre of resin bed in the resin phase. The volume of the resin bed is the volume of the resin beads and the void space about them. All of these studies were conducted in 7 M nitric acid solutions. In this extremely high ionic strength media it will be assumed that all the relevant activity coefficient ratios are constant. In 7 M nitric acid there is considerable resin invasion by the nitric acid so this assumption may not be too unreasonable even for the resin phase. However, with the above definition the non-exchange nitrate within the resin phase does not contribute to $[\overline{NO_3^-}]$.

If $[Pu_T]$ indicates the total concentration of all significant species of plutonium in the aqueous phase,

$$\begin{aligned}[Pu_T] = [Pu^{4+}] + [PuNO_3^{3+}] + \cdots + [Pu(NO_3)_6^{2-}]\\ + [HPu(NO_3)_5] + [HPu(NO_3)_6^-] + [H_2Pu(NO_3)_6]\end{aligned} \tag{6}$$

If the series of nitrate-complex dissociation quotients are defined by

$$k_n = \frac{[Pu(NO_3)_{n-1}^{5-n}][NO_3^-]}{[Pu(NO_3)_n^{4-n}]}, (n = 1, \ldots, 6) \tag{7}$$

and the acid dissociation quotients by

$$k_{mn} = \frac{[H_{m-1}Pu(NO_3)_n^{5-n-m}][H^+]}{[H_mPu(NO_3)_n^{4-n-m}]}, \quad (n = 5, m = 1; n = 6, m = 1, 2). \tag{8}$$

then Equation (6) takes the form

$$[\mathrm{Pu}_l] - [\mathrm{Pu(NO_3)_6^{2}}\ ]\left\{1 \quad \frac{k_6}{[\mathrm{NO_3}\ ]} + \frac{k_6 k_5}{[\mathrm{NO_3}\ ]^2} \right.$$

$$\left. , \frac{k_6 \quad k_1}{[\mathrm{NO_3}\ ]^6} \ ! \ \frac{k_6[\mathrm{H}\ ]}{k_{15}[\mathrm{NO_3}\ ]} \ , \ \frac{[\mathrm{H^+}]}{k_{16}} + \frac{[\mathrm{H^+}]^2}{k_{16}k_{26}}\right\} \quad (9)$$

$$[\mathrm{Pu(NO_3)_6^{2}}\ ]\ \{1/F_{\mathrm{Pu}}\}, \quad (10)$$

where I_{Pu}, the ionic fraction of plutonium as $\mathrm{Pu(NO_3)_6^{2-}}$, is a function only of $[\mathrm{NO_3}\ ]$ and $[\mathrm{H}\ ]$ and not of $[\mathrm{Pu}_l]$ For plutonium the definition of the distribution coefficient as given in Equation (1) becomes

$$\overline{[\mathrm{Pu}_l]} - D_I^{\ \mathrm{Pu}}[\mathrm{Pu}_T]$$

Since it is assumed that the only sorbing species of plutonium is $\mathrm{Pu(NO_3)_6^{2-}}$,

$$[\mathrm{Pu}_r] \quad \overline{[\mathrm{Pu(NO_3)_6^{2-}}]}, \quad (11)$$

and

$$\overline{[\mathrm{NO_3}\ ]} \quad c \quad 2\overline{[\mathrm{Pu(NO_3)_6^{2-}}]} \quad c \quad 2[\mathrm{Pu}_l]D_I^{\ \mathrm{Pu}} \quad (12)$$

where c is the equivalent capacity of the resin for anions It has a value of 1 16 mequ/ml of nitrate form resin in 7 M nitric acid $^{(14)}$
With equations (9), (10) (11) and (12) equation (5) becomes

$$K_{\mathrm{Pu}} - \frac{D_I^{\ \mathrm{Pu}}[\mathrm{NO_3}\ ]^2}{I_{\mathrm{Pu}}\{c - 2[\mathrm{Pu}_l]D_I^{\ \mathrm{Pu}}\}^2} \quad (13)$$

As $\overline{[\mathrm{Pu}_r]}$ approaches zero we can define an infinite-dilution distribution coefficient $(D_I^{\ \mathrm{Pu}})'$ by

$$D_I^{\ \mathrm{Pu}} \to (D_I^{\ \mathrm{Pu}})' \text{ when } \overline{[\mathrm{NO_3}\ ]} \to c$$

These conditions yield

$$K^{\mathrm{Pu}} = \frac{(D_I^{\ \mathrm{Pu}})\ [\mathrm{NO_3}\ ]^2}{F_{\mathrm{Pu}}c^2}. \quad (14)$$

With $[\mathrm{NO_3}\ ]$ constantly seven, equations (13) and (14) yield the quadratic

$$\{D_I^{\ \mathrm{Pu}}\}^2 \quad \frac{c}{[\mathrm{Pu}_l]}\left\{1 - \frac{c}{4[\mathrm{Pu}_T](D_I^{\ \mathrm{Pu}})}\right\} D_I^{\ \mathrm{Pu}} \quad \frac{c^2}{4[\mathrm{Pu}_r]^2} = 0 \quad (15)$$

Equation (15) can also be written

$$(D_I^{\ \mathrm{Pu}})' \quad D_I^{\ \mathrm{Pu}}\left\{\frac{c}{c \quad 2[\mathrm{Pu}_T]D_I^{\ \mathrm{Pu}}}\right\}^2 \quad (16)$$

Equation (16) was used to determine $(D_I^{\ \mathrm{Pu}})'$ with a measurement of $D_I^{\ \mathrm{Pu}}$ at as low a $[\mathrm{Pu}_T]$ as was analytically practical A value of 945 was found for $D_I^{\ \mathrm{Pu}}$ when $[\mathrm{Pu}_T]$ - 1 21 10^{-5} M which yields a value of 978 for $(D_I^{\ \mathrm{Pu}})'$ The results of other experimental measurements of $D_I^{\ \mathrm{Pu}}$ are shown in Fig, 2 along with the theoretical curve as calculated from equation (15) The point furthest to the left indicates a resin loading of 1 7 per cent, while those furthest to the right represent loadings of greater

---

[14] *Dowex Ion Exchange*, p 19, The Dow Chemical Co (1957, 1959)

than 99 per cent of capacity. While the resin shrinks about 25 per cent for these high loadings, it was assumed that the total capacity of the resin in a batch experiment was not altered. All resin volumes in this paper are based on the volume of the unloaded resin in 7 M nitric acid. The capacity of the resin for plutonium, 138 g Pu/l of unloaded resin, was calculated from the equivalent capacity of the resin for anions, assuming the plutonium is sorbed as a doubly-charged anion.

If the activity coefficients of all the species in both phases are indeed constant in the 7 M nitric acid, then a relation similar to equation (15) should hold for any species which is sorbed as a bivalent anion. For a general element A sorbed as a bivalent anion, the solution of equation (15) is

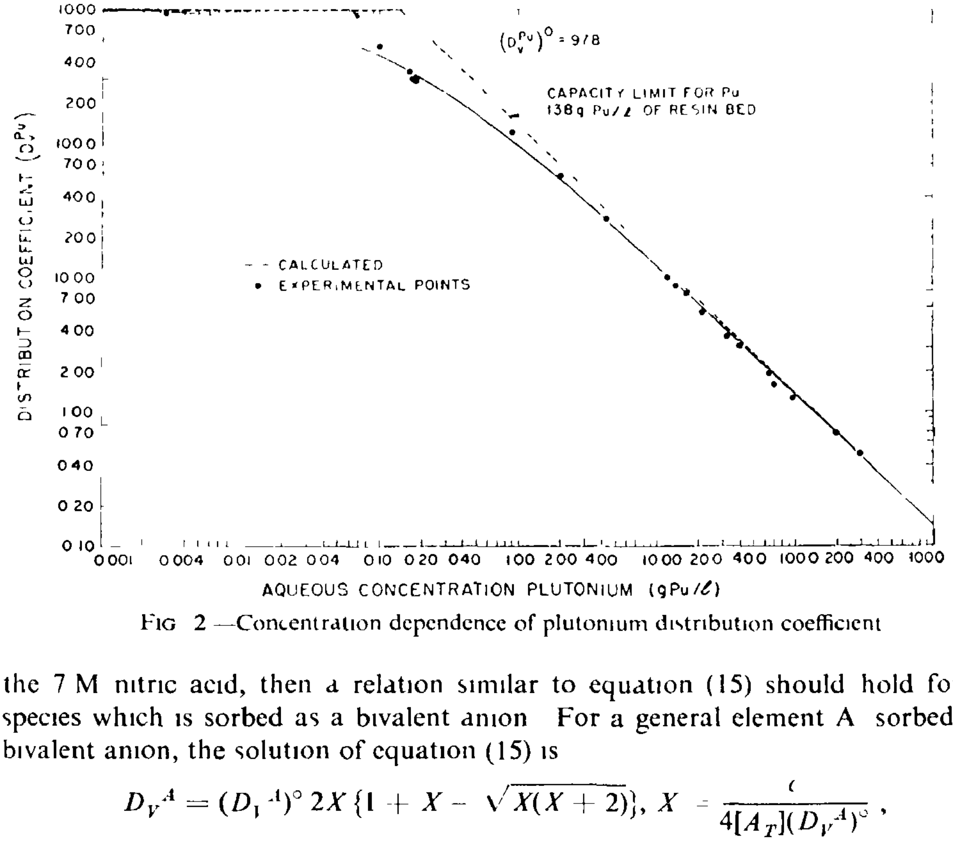


Fig. 2.—Concentration dependence of plutonium distribution coefficient.

$$D_V^A = (D_V^A)^\circ\, 2X\{1 + X - \sqrt{X(X+2)}\},\quad X = \frac{c}{4[A_T](D_V^A)^\circ}, \tag{17}$$

for a general element B, sorbed as a univalent anion, equation (17) takes the form

$$D_V^B = (D_V^B)^\circ \frac{c}{c + [B_T](D_V^B)^\circ}. \tag{18}$$

Equations (17) and (18) were tested for thorium (IV) and uranium (VI) which have been shown to be sorbed as $\mathrm{Th(NO_3)_6^{2-}}$ and $\mathrm{UO_2(NO_3)_4^{2-}}$ by Ryan[(9,10)] and for gold (III) which was assumed to be sorbed as $\mathrm{Au(NO_3)_4^-}$, since it has been shown to be sorbed as $\mathrm{AuCl_4^-}$ from hydrochloric acid.[(5)] The results are shown in Table 1.

Carroll[(15)] has investigated the sorption of thorium from 7 M nitric acid on Permutit $\mathrm{SK(20\text{–}50)NO_3^-}$. Equation (17) was applied to these data, using $c = 4.5$ milliequivalents per oven-dry gramme of resin and substituting for D_V^{Th}

$$K_d^{\mathrm{Th}} \doteq \frac{\text{mg Th/oven-dry gramme of resin}}{\text{g Th/litre of solution}}$$

[(15)] J. L. Carroll, *AEC Pub. HW*-**70536** (1961).

TABLE 1.—DISTRIBUTION COEFFICIENTS ON DOWEX 1X4 FROM 7 M NITRIC ACID

Element	Aqueous-phase concentration (g/l.)	Fraction of the resin loaded	Distribution coefficient Calculated	 experimental
Au(III)	0.0355	0.017	114	114*
Au(III)	0.335	0.21	99	92
AU(III)	5.91	0.78	30	25
Th(IV)	0.111	0.077	87	87†
Th(IV)	0.459	0.30	65	50
Th(IV)	2.09	0.40	30	37
U(VI)	0.37	0.011	4.6	4.6‡
U(VI)	5.7	0.20	3.4	3.0
U(VI)	7.3	0.21	3.2	3.0
U(VI)	9.7	0.23	2.9	2.8
U(VI)	13.4	0.24	2.6	2.7

* Experiment used to calculate (D_I^{Au}) = 116.
† Experiment used to calculate (D_I^{Th}) = 102.
‡ Experiment used to calculate (D_I^{U}) = 4.7.

The results are shown in Table 2.

TABLE 2.—DISTRIBUTION COEFFICIENTS OF THORIUM ON PERMUTIT SK

Aqueous phase concentration of thorium (g/l.)	Equilibrium temperature (°C)	Distribution coefficient, K_d^{Th} calculated	 experimental
0.175	64	86	86*
0.443	64	80	78
0.454	64	79	76
1.72	64	59	66
1.78	64	59	65
9.45	64	26	35
9.52	64	26	33
0.175	25	124	124†
0.454	25	111	109
1.78	25	75	78
9.52	25	29	40

* Experiment used to calculate (K_d^{Th}) = 91 for 64°C.
† Experiment used to calculate (K_d^{Th}) = 135 for 25°C.

The constant products of the ion-exchange equilibrium constant and the ionic fraction, *KF*, were determined for these elements. For plutonium, thorium and uranium the relationship,

$$K_I F_I = \frac{19.9 D_I^{4}}{\{c - 2[A_T]D_I^{4}\}^2}, \tag{19}$$

was derived from equation (13). It was interpolated from Raman-spectra data[(16)]

---

(16) H. S. HARNED and B. B. OWEN, *Physical Chemistry of Electrolytic Solutions*, p. 582. Reinhold, New York (1958).

that $[NO_3^-] = 4\ 46$ in 7 M nitric acid For the univalent gold this equation takes the form

$$K_B F_B = \frac{4\ 46 D_v^B}{c - [B_T] D_v^B} \tag{20}$$

An average of all the experimental data was used, except for concentrations of plutonium above 25 g/l where $c - 2[Pu_T] D_V^{Pu}$ becomes too small compared to the error in the analyses The results of these calculations are shown in Table 3 The average deviation from the mean is also given While the deviation was considerable, there was no trend in the results with concentration

TABLE 3 —ION EXCHANGE-IONIC FRACTION PRODUCT CONSTANT

Element	KF
Au	$(3 \pm 1)\ 10^2$
U	65 ± 6
Th	$(1\ 9 \pm 0\ 8) \times 10^3$
Pu	$(1\ 3 + 0\ 3)\ 10^4$

The application of equations (17) and (18) requires one distribution coefficient measurement as near as possible to infinite dilution, a knowledge of the charge on the sorbing anion and the capacity of the resin The distribution coefficients for many species are given in Fig 3 All of these measurements were made at a sufficiently low

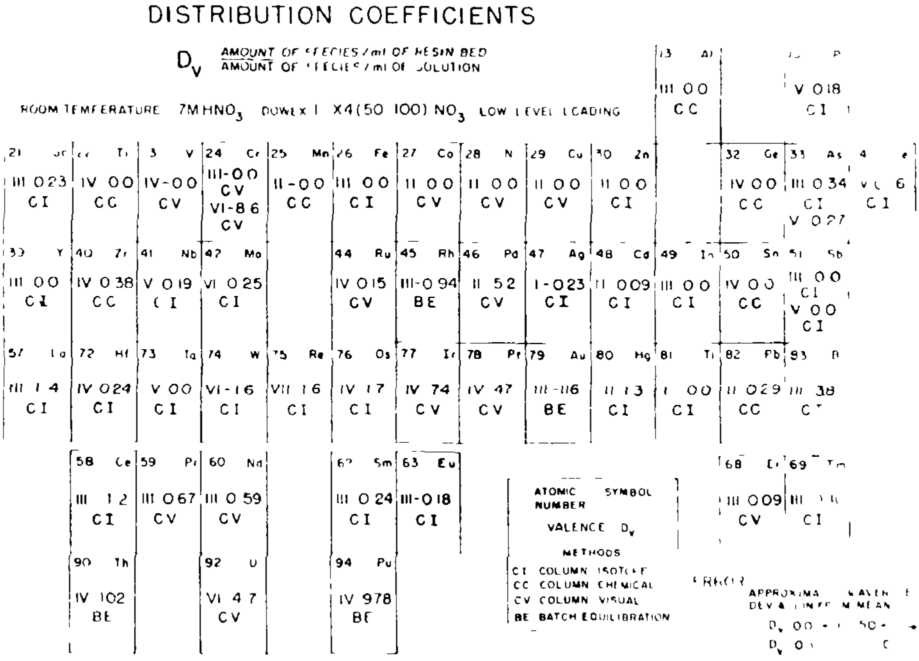

DISTRIBUTION COEFFICIENTS
D_V = AMOUNT OF SPECIES/ml OF RESIN BED / AMOUNT OF SPECIES/ml OF SOLUTION
ROOM TEMPERATURE 7M HNO$_3$ DOWEX I X4(50 100) NO$_3$ LOW LEVEL LOADING
13 Al III 0 0 CC
15 P V 0 18 CI
21 Sc III 0 23 CI
22 Ti IV 0 0 CC
23 V IV-0 0 CV
24 Cr III-0 0 CV VI-8 6 CV
25 Mn II-0 0 CC
26 Fe III 0 0 CI
27 Co II 0 0 CV
28 Ni II 0 0 CV
29 Cu II 0 0 CV
30 Zn II 0 0 CI
32 Ge IV 0 0 CC
33 As III 0 34 CI V 0 27
34 Se VI 6 CI
39 Y III 0 0 CI
40 Zr IV 0 38 CC
41 Nb V 0 19 CI
42 Mo VI 0 25 CI
44 Ru IV 0 15 CV
45 Rh III-0 94 BE
46 Pd II 5 2 CV
47 Ag I-0 23 CI
48 Cd II 0 09 CI
49 In III 0 0 CI
50 Sn IV 0 0 CC
51 Sb III 0 0 CI V 0 0 CI
57 La III 1 4 CI
72 Hf IV 0 24 CI
73 Ta V 0 0 CI
74 W VI-1 6 CI
75 Re VII 1 6 CI
76 Os IV 1 7 CI
77 Ir IV 7 4 CV
78 Pt IV 4 7 CV
79 Au III-116 BE
80 Hg II 1 3 CI
81 Tl I 0 0 CI
82 Pb II 0 29 CC
83 Bi III 3 8 CI
58 Ce III 1 2 CI
59 Pr III 0 67 CV
60 Nd III 0 59 CV
62 Sm III 0 24 CI
63 Eu III-0 18 CI
68 Er III 0 09 CV
69 Tm III CI
90 Th IV 102 BE
92 U VI 4 7 CV
94 Pu IV 978 BE
ATOMIC NUMBER SYMBOL
VALENCE D_V
METHODS
CI COLUMN ISOTOPE
CC COLUMN CHEMICAL
CV COLUMN VISUAL
BE BATCH EQUILIBRATION
ERROR
APPROXIMATE AVERAGE DEVIATION FROM MEAN
D_V 0 0 - 1 50 -
D_V 0

FIG 3 —Distribution coefficients

degree of resin loading so that the correction to infinite dilution is probably within the experimental error of the measurement. The quantity $D_I + i$ (see equation 3) was measured for each species in the column experiments. Eighteen results were near 0.54, and none were significantly lower. An average of these eighteen measurements with the assumption that they represented distribution coefficients of zero gave a value to i of 0.54 with an average deviation from the mean of 0.02. One would expect a value of about 0.4 for i assuming hexagonally closest-packed, uniform beads. The high value obtained experimentally is probably caused by the narrow column relative to a single bead diameter. Those distribution coefficients listed as 0.0 in Fig. 3 represent measurements of $D_{I^-} + i$ of less than 0.62.

The charge on the sorbing anion is not so easily measured. The methods for determining ionic charge by ion-exchange techniques were reviewed by SALMON(17); the methods of RYAN(10,11) appear satisfactory for these applications.

While the data in Fig. 3 suggest several separations applications, care must be taken in quantitatively predicting separation factors from the data, especially for applications at the higher degrees of resin loading. Preliminary investigations indicate that macro-loading distribution coefficients of several elements in a mixed system may not be simply related to the individual infinite-dilution distribution coefficients.

Acknowledgements—The author wishes to thank the personnel of this Laboratory in Groups CMB-1 who performed the analyses, and CMB-7, who provided the instrumentation. Mr. W. D. MCNEESE designed and built the column scanning device.

(17) J. F. SALMON, *Rev. Pure Applied Chem.* **6**, 24 (1956).

J Inorg Nucl Chem, 1963, Vol 25 pp 719 to 740 Pergamon Press Ltd Printed in Northern Ireland

NOTES

The separation of ^{239}Np

(*Received* 4 *November* 1962 *in revised form December* 1962)

^{239}Np is KNOWN to be produced by irradiation of uranium with slow neutrons Isolation demands separation from the fission products and uranium This note briefly reports the results of an investigation of the separation of ^{239}Np A more detailed account appears elsewhere (1 3)

Extraction procedure

This procedure involves only solvent extraction techniques It is based on the selective extraction of Np(VI) by diethyl ether from nitric acid solutions in the presence of a salting out agent and on the differences in the behaviour of Np(VI) and Np(V)

The efficient extraction of Np(VI) by diethyl ether permits the isolation ^{239}Np even at a low nitric acid concentration (e g 0 2 M), in the presence of calcium nitrate (about 3 5 m/l) as salting out agent The fission products mostly remain in the aqueous phase Further purification of neptunium is achieved by washing the extract with an aqueous solution, containing an oxidant Then neptunium is stripped with an aqueous solution containing a salting out agent, to prevent stripping of the uranium, and hydrazine nitrate in nitric acid, hydrazine reduces neptunium in the cold to the unextractable pentavalent state The second extraction, carried out after oxidation, ensures ^{239}Np of high purity The procedure is described in detail elsewhere(3) A similar procedure based on methyl-isobutylketone has been subsequently reported(4)

Separation of ^{239}Np *using the recoil of the fission product nuclei*

To separate ^{239}Np use can be made of the recoil of the nuclei of the fission products The nuclei of the energetic fragments travel rather a long way in the parent compound, for instance 8 μ in U_3O_8 On the other hand the range of ^{239}U and ^{239}Np is negligible By using particles of the parent compound of a size smaller than the range of the fission products it is possible to separate the parent compound from the activity due to the fission products and to leave only the activity due only to ^{239}Np, after decay of the ^{239}U The recoil of the fission product nuclei has already been used to isolate fission products(5, 6) WOLFGANG(5) has also pointed to the possibility of extracting actinides

For the irradiation we have made use of uranium dioxide with the ^{235}U content reduced to 0 4 per cent Calcium carbonage was used as a filler An even distribution of the UO_2 particles, of ~2 μ in diameter, in the bulk of the calcium carbonate was attained by precipitating the latter from a saturated solution of calcium nitrate in which the UO_2 particles had been previously distributed so that the bulky precipitate entrained particles of dioxide After drying the precipitate was irradiated in a reactor The separation of the filler after irradiation was effected by dissolving calcium carbonate in hydrochloric acid Details are given in reference 1

---

(1) YU A ZOLOTOV and I P ALIMARIN, *Atomnaya Energiya* 6, 70 (1959)
(2) YU A ZOLOTOV and D NISHANOV, *Radiokhimiya* 4, 241 (1962)
(3) L S PALSHIN and YU A ZOLOTOV, *Radiokhimiya* 1, 482 (1959)
(4) W J MAECK, G L BOOMAN, M G ELLIOTT and J E REIN *Analyt Chem* **32**, 605 (1960)
(5) R WOLFGANG, *J Inorg Nucl Chem* **2**, 180 (1956)
(6) R HENRY and C HIRCZID, Report at the International Conference on the Use of Radioactive Isotopes in Scientific Research Paris 1957

Chromatographic procedure

An ion-exchange separation of neptunium has been reported [7,8] In our work use was made of cationite CU-2 (similar in properties to Dowex-50) with 1 M nitric acid as eluant On a column 30 35 cm in length and 0 5 cm in diameter with cationite grains of 0 1 mm average diameter and at 0 2 ml min Np (V) is eluted very quickly and appears as a sharp peak on the elution curve Preliminary treatment of the solution to convert neptunium to the pentavalent state is not necessary if the starting solution contains only Np(V) and Np(VI) as the Np(VI) is reduced to the pentavalent one by the cationite itself Under these conditions uranium is eluted much later and the bulk of the fission products remain on the resin Purification from the eluted fission products (Ru, Te, I and possibly Cs) is carried out by extracting neptunium with diethyl ether after its oxidation to Np(VI)

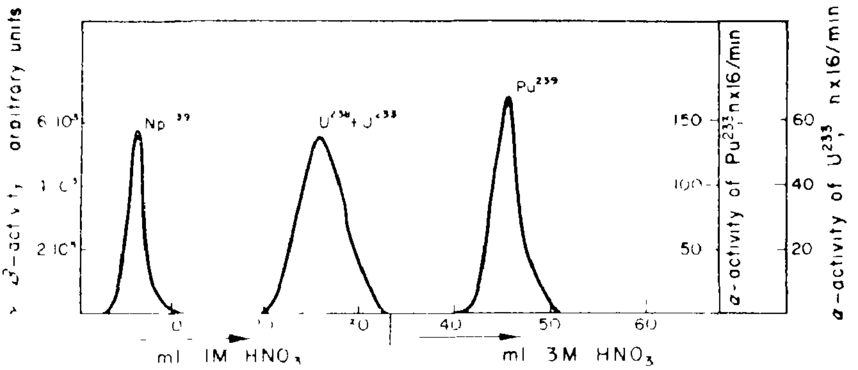


FIG 1 Separation of neptunium (V), uranium (VI) and plutonium (IV) on elution with 1 and 3M nitric acid

This procedure can also be used to separate ^{237}Np, Pu and U after treating the solution with sodium nitrite to obtain Np(V) and Pu(IV) Plutonium is eluted with 3 M HNO_3 Fig 1 shows that such a separation may be successful As to particulars see reference 2

V I Vernadsky Institute of Geochemistry and Analytical Chemistry,
Academy of Sciences of the USSR Moscow, U S S R

YU A ZOLOTOV
I P ALIMARIN

[7] R M DIAMOND, K STREET and G T SEABORG, *J Amer Chem Soc* **76**, 1461 (1954)

[8] G JOHANSSON *Svensk Kem Tidskr* **65**, 79 (1953)

[9] F JOLIOT, *C R Acad Sci, Paris* **218**, 733 (1944)

On the formation of ternary M(II)-citrate-imidazole complexes

(*Received* 22 *October* 1962)

A SURVEY of the literature shows that binary metal complexes of citrate and of imidazole have been extensively studied[1 4], however, nothing has been reported on ternary metal-citrate-imidazole complexes As part of a research program on mixed ligand studies, this note presents the results on the formation of several ternary M(II)-citrate-imidazole complexes

[1] J BJERRUM, G SCHWARZENBACH and L G SILLEN, *Stability Constants*, Special Publication No 6, Part I *Organic Ligands*, The Chemical Society, London, 1957

[2] R B MARTIN and J T EDSALL, *J Amer Chem Soc* **80**, 5033 (1958)

[3] J T LANE and K P QUINLAN, *J Amer Chem Soc* **82**, 2995 (1960)

[4] N C LI, W M WESTFALL, A LINDENBAUM, J M WHITE and J SCHUBERT *J Amer Chem Soc* **79**, 5864 (1957)

We have used a liquid anion-exchange and a polarographic method for the purpose of demonstrating the existence of M(II) citrate-imidazole complexes. Using a pH titration method, we have also determined the formation constants of several M(II)-citrate-imidazole and M(II)-citrate-benzimidazole complexes, where M(II) is Co(II), Ni(II) or Cd(II).

Experimental

Materials. High activity Co-60 was obtained from Oak Ridge National Laboratory in the form of cobaltous chloride in HCl solution. The liquid anion exchanger, "Aliquat 336", a high molecular weight, water-insoluble quarternary ammonium chloride (General Mills, Minneapolis, Minn.) was used. All other chemicals were of C.P. quality.

Procedure. In liquid ion exchange experiments, the aqueous phase normally was prepared to contain (a) Co-60 in concentrations of the order of 10^{-6} M, (b) varying concentrations of imidazole, each half neutralized with hydrochloric acid, and (c) sodium citrate in varying concentrations. The benzene phase contained "Aliquat 336" (5.8 wt %) in the chloride form. Equal volumes of aqueous and organic phases were then placed in glass-stoppered erlenmeyer flasks, shaken at 25 ± 0.2° overnight, and allowed to settle for 2 hr at 25°. Aliquots from both phases were removed for counting of Co-60 in a NaI(Tl) scintillation counter. The precision attained in distribution coefficients was about ± 2 per cent.

Polarographic current-voltage curves were made with a Fisher Electropode. All potentials were measured at 25° against a saturated calomel electrode (S.C.E.) in the manner described by Li and Chen.(5)

pH measurements were made at 25° in a nitrogen atmosphere, using a conventional calomel-glass electrode couple with a Beckman Model G pH meter.

Results and discussion

(A) *Liquid anion-exchange studies.* Fig. 1 shows plots of $1/D$ vs. 1/(total citrate) for four different imidazole concentrations, where D is distribution coefficient and is defined by the equation

$$D = \frac{\text{total } M(\text{II}) \text{ conc. in organic phase}}{\text{total } M(\text{II}) \text{ conc. in aqueous phase}} \tag{1}$$

Plots of $1/D$ vs. concentration of free base imidazole (Im), for four different concentrations of sodium citrate are shown in Fig. 2. The results may be interpreted in the following manner. In the absence of imidazole, the distribution coefficient is given by the expression

$$D = \frac{(M\text{Cit}^-)_{\text{org}}}{(M^{++}) + (M\text{Cit}^-)} \tag{2}$$

while in the presence of imidazole

$$D = \frac{(M\text{Cit}^-)_{\text{org}}}{(M^{++}) + (M\text{Cit}^-) + (M\text{CitIm}^-) + (M\text{CitIm}_2^-) + (M\text{Im}^{++}) + (M\text{Im}_2^{++})} \tag{3}$$

With the introduction of the following equations

$$\begin{aligned} D' &= (M\text{Cit}^-)_{\text{org}}/(M\text{Cit}^-) \\ k_i &= (M\text{CitIm}_i^-)/(M\text{Cit}^-)(\text{Im})^i \\ k &= (M\text{Cit}^-)/(M^{++})(\text{Cit}^{-3}) \\ k_n' &= (M\text{Im}_n^{++})/(M^{++})(\text{Im})^n \end{aligned} \tag{4}$$

the following equations result

$$\begin{aligned} (1/D^0) &= (1/D') + (1/D'k)(1/(\text{Cit}^{-3})) \\ (1/D) &= (1/D^0) + \{[k_1(\text{Im})]/D'\} + \{[k_2(\text{Im})^2]/D'\} \\ &\quad + \{[k_1'(\text{Im})]/[D'k(\text{Cit}^{-3})]\} + \{[k_2'(\text{Im})^2]/[D'k(\text{Cit}^{-3})]\} \end{aligned} \tag{5}$$

---

(5) N. C. Li and M. C. Chen, *J. Amer. Chem. Soc.* **80**, 5678 (1958).

We must also consider the citrate ion itself may be absorbed and if under the experimental conditions, a constant fraction F of the total citrate, A_t, remains in the aqueous phase, then equation (5) becomes

$$(1/D) = \{[1 + k_1(\text{Im}) + k_2(\text{Im})^2]/D'\} + (1/A_t)\{[1 + k_1'(\text{Im}) + k_2'(\text{Im})^2]/(FD'K)\} \qquad (6)$$

$$(1/D) = (1/D') + [1/(FD'K)](1/A_t) + \{(k_1/D') + [k_1'/(FD'KA_t)]\}(\text{Im}) + \{(k_2/D') + [k_2'/(FD'K)](1/A_t)\}(\text{Im})^2 \qquad (7)$$

Equation (6) predicts that at constant imidazole concentration, a plot of $1/D$ vs $1/A_t$ should yield a straight line and that both the intercept and slope increase with increase in imidazole concentration

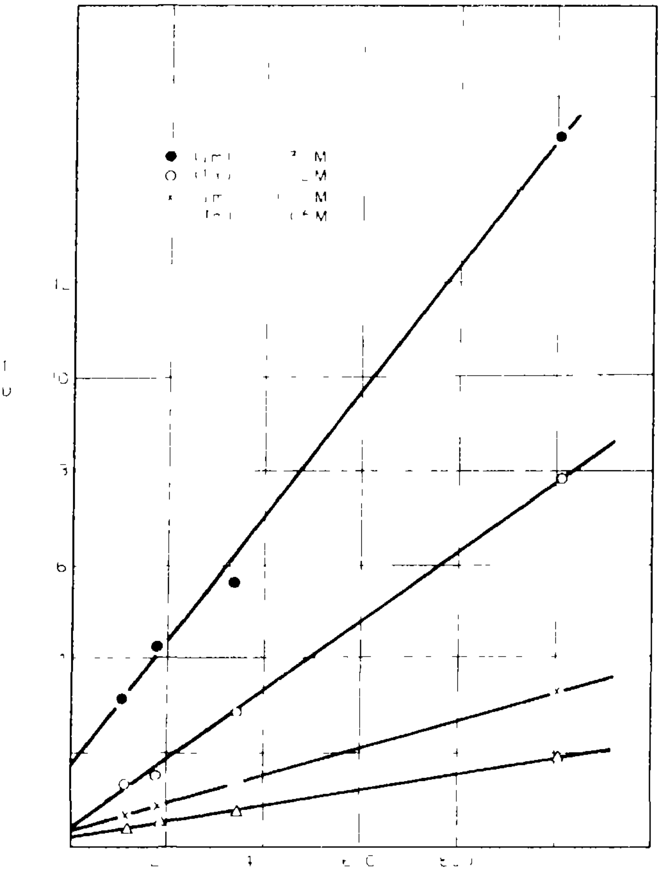


FIG. 1 – Dependency, citrate concentration on the extraction of Co(II) in citrate-imidazole mixtures by Aliquat 336

Equation (7) shows that at constant total citrate concentration, a plot of $1/D$ vs (Im) should yield a curve, and that both the slope and intercept increase with decrease in total citrate concentration Figs 1 and 2 show that the experimental data are in agreement with the predictions of equations (6) and (7) Moreover, equation (7) can be rearranged to yield

$$y = \frac{(1/D) - I}{(\text{Im})} = a + b(\text{Im}) \qquad (8)$$

where I is the intercept of a $1/D$ vs (Im) plot at constant value of A_t in Fig 2, a and b are the coefficients of (Im) and $(\text{Im})^2$, respectively, in equation (7) A plot of y vs (Im) therefore, at constant A_t, should yield a straight line, and this is the case for our anion-exchange data. We have thus established that in the region 0.001–0.01M sodium citrate and 0.005–0.03M imidazole, two ternary complexes CoCitIm and $CoCitIm_2^-$, are present in solution together with the binary complexes $CoIm^{++}$ and $CoIm_2^{++}$. Since the fraction of citrate, Γ, remaining in the aqueous phase was not determined experimentally, we have not attempted to evaluate the formation constants of the ternary complexes by the anion-exchange method.

(B) *Polarographic study of Cd(II)-citrate-imidazole complex.* KOLTHOFF and LINGANE[6] have given the following expression for the polarographic half-wave potentials of a M(II) metal ion

$$(E_{\frac{1}{2}})_c - (E_{\frac{1}{2}})_s = -0.030 \log K_f - p\ 0.030 \log (A) \qquad (9)$$

where $(E_{\frac{1}{2}})_c$ and $(E_{\frac{1}{2}})_s$ are the half-wave potentials in the presence and in the absence of a ligand, A, respectively. K_f is the equilibrium constant of the reaction $M^{2+} + pA = MA_p$. In the simultaneous presence of two ligands A and B, forming a ternary complex MA_pB_q, the expression for the half-wave potential would be

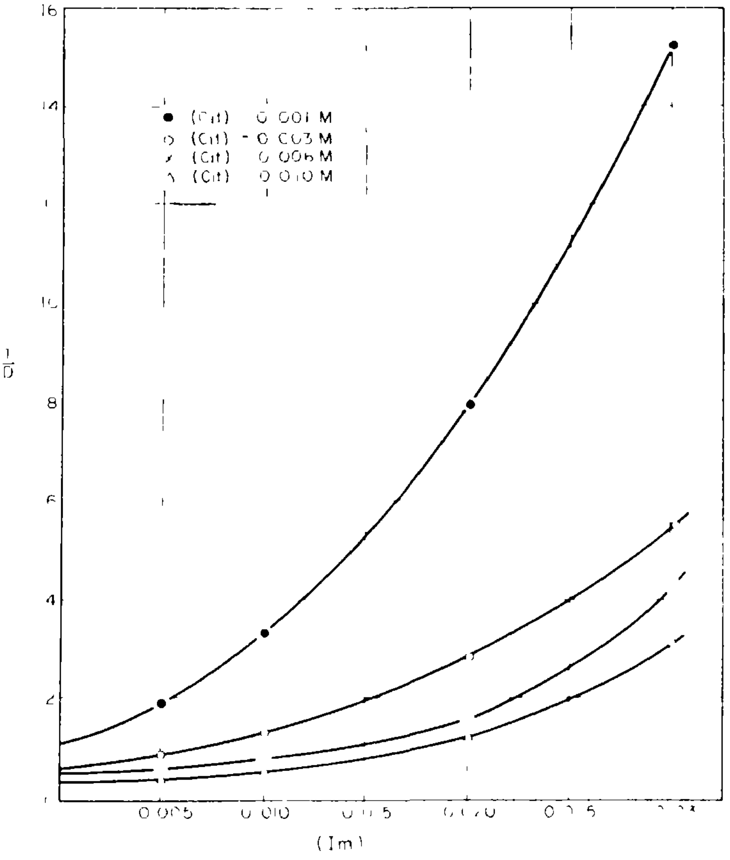


FIG. 2.—Dependency, imidazole concentration (Im) on the extraction of Co(II) in citrate-imidazole mixtures by Aliquat 336.

$$(E_{\frac{1}{2}})_c - (E_{\frac{1}{2}})_s = -0.030 \log K_{AB} - p\ 0.030 \log (A) - q\ 0.030 \log (B) \qquad (10)$$

where K_{AB} is the equilibrium constant of the reaction

$$M^{+2} + pA + qB = MA_pB_q$$

---

[6] I. M. KOLTHOFF and J. J. LINGANE, *Polarography*, Interscience, New York (2nd ed.), 1952.

For solutions containing $5 \times 10^{-4}M$ Cd(NO$_3$)$_2$, 0.005% gelatin as maximum suppressor, 0.15M KNO$_3$, 0.03M sodium citrate, B, and varying concentrations of imidazole, A, the electrode reaction is reversible. A plot of $E\frac{1}{2}$ vs. −log (A), in the concentration range (A) = 0.1–0.5M, is linear, the slope being 0.09. From equation (10), it is seen that $p = 3$. For solutions containing $5 \times 10^{-4}M$ Cd(NO$_3$)$_2$, 0.005% gelatin as maximum suppressor, 0.15M KNO$_3$ and sodium citrate varying from 0.01–0.05M, the slope of a $E\frac{1}{2}$ vs. log (Citrate) plot is 0.03, so that Cd(II) forms a monocitrate complex in this concentration range. In the presence of 0.03M sodium citrate and imidazole varying from 0.1–0.5M, therefore, the complex is Cd Cit Im$_3$. Li *et al.*,(7) have shown that in the absence of citrate, the complex is CdIm_4^{++} when the imidazole concentration is above 0.08M. In the presence of 0.03M sodium citrate, therefore, one mole of citrate displaces one mole of imidazole in the tetra-imidazole complex.

From our polarographic data and equation (10), log K_{AB} for the CdCitIm$_3$ complex was calculated to be 8.8. The value of log K for the formation of the CdCit complex has been reported to be 3.98(8), so that log k_3, the logarithm of the equilibrium constant of the following reaction

$$\text{CdCit} + 3\,\text{Im} \rightleftharpoons \text{CdCitIm}_3$$

is easily calculated to be 8.8 − 3.98 or 4.8.

TABLE 1. FORMATION CONSTANTS OF SEVERAL BINARY AND TERNARY COMPLEXES

Ternary complexes	log k_1	Binary complexes	log K_1
CdCit(imidazole)	2.50	Cd(imidazole)$^{++}$	2.80(11)
NiCit(imidazole)	3.10	Ni(imidazole)$^{++}$	3.27(12)
CoCit(imidazole)	2.48	Co(imidazole)$^{++}$	2.58
NiCit(benzimidazole)	2.11	Ni(benzimidazole)$^{++}$	2.24
CoCit(benzimidazole)	1.62	Co(benzimidazole)$^{++}$	1.66

(C) *pH study of imidazole and benzimidazole complexes.* For titration with a standard alkali, the solution was normally prepared to contain (a) 0.01M nitrate or chloride salt of the divalent metal, (b) 0.01M sodium citrate, (c) 0.01M imidazolium or benzimidazolium chloride, (d) sufficient sodium chloride to keep the total ionic strength of the initial solution 0.15. The data were treated in the manner described by EDSALL *et al.*,(9) except that $\bar{v}$ now refers to the concentration of bound imidazole or benzimidazole per mole of M(II) citrate, and the formation constant is now k_1 (equation 4 of this paper). This treatment is valid because equimolar amounts of M(II) salt and sodium citrate were used and the formation constant of the M(II) citrate complex is so high(1) that practically all of the M(II) and citrate ions in the initial solution were bound in the M(II)-monocitrate complex. During the titration therefore, we may consider that the alkali added is reacting with the hydrogen ion set free by the following reaction

$$\text{M(II) citrate}^- + \text{HIm}^+ = \text{MCitIm}^- + \text{H}^+$$

where Im is imidazole or benzimidazole.

Table 1 lists the formation constants, k_1, of several ternary complexes obtained by pH titrations. For comparison, the formation constants, K_1' (equation 4), are included. It will be noticed that for each M(II), k_1 is always smaller than K_1'. This trend has been observed by SCHAAP and MCMASTERS(10) for M(II) complexes with oxalate and ethylenediamine, and has been ascribed to statistical and entropy factors

---

(7) N. C. LI, J. M. WHITE and E. DOODY, *J. Amer. Chem. Soc.* **76**, 6219 (1954).

(8) N. C. LI, A. LINDENBAUM and J. M. WHITE, *J. Inorg. Nucl. Chem.* **12**, 122 (1959).

(9) J. T. EDSALL, G. FELSENFELD, D. S. GOODMAN and F. R. N. GURD, *J. Amer. Chem. Soc.* **76**, 3054 (1954).

(10) W. B. SCHAAP and D. L. MCMASTERS, *J. Amer. Chem. Soc.* **83**, 4699 (1961).

(11) C. TANFORD and M. L. WAGNER, *J. Amer. Chem. Soc.*, **75**, 434 (1953).

(12) N. C. LI, T. L. CHU, T. FUJII and J. M. WHITE, *J. Amer. Chem. Soc.* **77**, 859 (1955).

Acknowledgement—The authors are indebted to the U S Atomic Energy Commission for support of this work through Contract No AT-(30-1)-1922

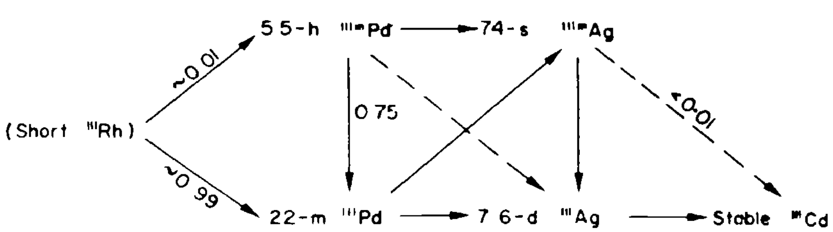
Department of Chemistry, Duquesne University
Pittsburgh 19, *Pennsylvania*

P TANG
N C LI

Relative yields of ^{111}Pd and ^{111m}Pd in the decay of ^{111}Rh

(*Received* 29 *October* 1962)

THE PUBLISHED data on the decay chain of mass number 111 is the following (1)



A knowledge of the relative yields of ^{111}Pd and ^{111m}Pd gives an indication of the branching ratio in the decay of the short-lived parent ^{111}Rh This note describes the results of determination of the ratio of cumulative yields of ^{111}Pd and ^{111m}Pd, in neutron fission of natural uranium

Experimental

The ratio ^{111}Pd/^{111m}Pd was obtained by determining separately the ^{111}Ag due to both ^{111}Pd and ^{111m}Pd together, and the ^{111}Ag due to ^{111m}Pd alone, taking advantage of the large difference in the half-lives of the two palladium isomers

About 1 g of natural uranium metal was irradiated by a neutron flux of 3×10^{11}, in the swimming pool reactor "Apsara" and dissolved in 6 M hydrochloric acid and a few drops of 30 per cent hydrogen peroxide The irradiation time varied from 30 min to 1 hr The solution was divided into two equal fractions Fraction I was set aside after adding sufficient ammonium carbonate to keep the uranium in solution and 20 mg of silver carrier as silver ammonia complex Silver was purified after the complete decay of ^{111}Pd and ^{111m}Pd, and ^{111}Ag was assayed (Sample I)

Fraction II was treated as follows to determine the ^{111}Ag formed by the decay of ^{111m}Pd 20 mg of silver carrier was added as silver ammonia complex after complexing uranium with ammonium carbonate After 6 hr during which the 22-m ^{111}Pd completely decayed to ^{111}Ag, silver activity was removed by eight silver chloride scavengings The time of last scavenging was noted as it represented the starting time for the growth of ^{111}Ag from ^{111m}Pd Again 20 mg of silver carrier was added as the ammonia complex, after complexing the uranium with ammonium carbonate After the complete decay of 5 5-*h* ^{111m}Pd, silver was purified and ^{111}Ag was assayed (Sample II-a)

In this procedure, there are two possible sources of error, one due to solubility of silver chloride and the other due to adsorption of palladium in tracer concentration on silver chloride The ratio will be much lower than the true value if, even after eight silver chloride scavengings, appreciable amount of ^{111}Ag remains in solution To check this, a separate experiment was carried out in which silver chloride was successively precipitated from a solution containing μc quantities of ^{110}Ag and counting the silver samples individually It was found that three silver chloride precipitations removed all the ^{110}Ag from the solution, showing that the solubility of silver chloride does not introduce a significant error in the value of ^{111}Pd/^{111m}Pd The ratio will be much higher than the true value, if any ^{111m}Pd was lost by adsorption on silver chloride during the large number of silver chloride scavengings To investigate this, a few experiments were carried out in which fraction II was treated by a procedure slightly different from the one given above

---

(1) KATCOFF, S , *Nucleonics* **18**, 201 (1960)

Twenty mg of palladium carrier was added to fraction II and palladium was separated by standard radiochemical procedure, after the complete decay of 22-m ^{111}Pd The time of last silver chloride scavenging (about six hours after the end of irradiation) was noted The chemical yield of palladium was determined by weighing it as its dimethyl glyoxime complex, $Pd(DMG)_2$ The $Pd(DMG)_2$ was dissolved in 10 M ammonium hydroxide and 20 mg of silver carrier was added as silver ammonia complex After the complete decay of 5 5-*h* ^{111m}Pd silver was purified as before (Sample II-b) The agreement of the values for the ratio calculated from samples II-a and II-b, together with the results of the solubility experiment shows that no appreciable error is introduced by any adsorption of palladium tracer on silver chloride

Assay of ^{111}Ag of the sample was carried out using a beta proportional counter, after the decay of the 3 12-*h* ^{112}Ag The activities of the samples II-a and II-b are due to ^{111}Ag, formed by the decay of a fraction of the initial amount of ^{111m}Pd alone The ^{111}Ag activity corresponding to the initially formed ^{111m}Pd was calculated by correcting the counting rate, for the decay of ^{111m}Pd from the end of irradiation to the last silver chloride scavenging, for the chemical yield of silver (for the chemical yield of palladium also for sample II-b) and also for the growth and decay of ^{111}Ag From the counting rate of sample I ^{111}Ag activity due to ^{111}Pd and ^{111m}Pd together was calculated by applying corrections for the chemical yield of silver and for the growth and decay of ^{111}Ag (sample I contained ^{111}Ag formed directly in fission also, but calculation on the basis of equal charge displacement hypothesis$^{(2)}$ indicates that it is of the order of 10^{-2} per cent of the total ^{111}Ag) As the ratio ^{111}Pd/^{111m}Pd was calculated from the ^{111}Ag activities counting efficiencies of ^{111m}Pd and ^{111}Pd were not required

TABLE 1

Expt No	1	2	3	4	5	6	7	Mean
Sample used	II-a	II-a	II-a	II-a	II-a	II-b	II-b	
^{111}Pd/^{111m}Pd	110	119	121	123	120	110	130	119 7

Results and conclusions

The results are given in Table I The ratio of ^{111}Pd/^{111m}Pd in the neutron fission of natural uranium was determined to be 119 7 This ratio of the cumulative yields of ^{111}Pd and ^{111m}Pd may be taken as a very approximate value for the branching ratio in the beta decay of ^{111}Rh, as the fractional chain yield of mass number 111 at palladium calculated on the basis of equal charge displacement hypothesis$^{(2)}$ is not insignificant and comes out to be about 7 per cent Further, the value will have a larger uncertainty if ^{111m}Ag decays directly to stable ^{111}Cd to an extent significantly larger than 1 per cent indicated in the decay scheme$^{(1)}$ The value 119 ± 7 compares well with the approximate value (about 100)* given in KATCOFF's summary of fission yields $^{(1)}$ Determination of the independent yields of ^{111}Pd and ^{111m}Pd would be useful but is very difficult, if not impossible, because of the very short half-life of ^{111}Rh

Acknowledgements –The authors are grateful to Dr G A WELCH and Dr H D SHARMA for their helpful criticism and continued interest in the work and to Professor A C WAHL for his valuable suggestions

Radiochemistry and Isotope Division
Atomic Energy Establishment, Trombay
Bombay–73

M V RAMANIAH
K RENGAN
N RAVINDRAN

---

* It is not clear whether this is an experimental or predicted value

(2) PAPPAS, A C AECU 2806, 1953

X-ray diffraction data on hydrated uranium peroxide

(*Received* 24 *December* 1962)

IT HAS been found recently[1] that two different hydrates of uranium peroxide can be obtained from the precipitate, formed by the addition of hydrogen peroxide to aqueous solutions containing uranyl ions. When this precipitate is dried at temperatures below 40°C $UO_4 \cdot 4H_2O$ is formed, above 70°C this is converted to $UO_4 \cdot 2H_2O$. The thermal decomposition of these hydrates has been studied by CORDFUNKE *et al.*[2,3]

This note gives the results of a preliminary investigation by X-ray diffraction on the hydrates of uranium peroxide. The diffraction patterns were obtained with a Philips diffractometer, using CuKα-radiation ($\lambda = 1.5418$ Å).

The compounds were prepared by dropwise addition of a 5% hydrogen peroxide solution to a 0.1 molar solution of uranyl nitrate, acidified with concentrated nitric acid. In this strongly acid medium the precipitation is delayed resulting in a product with better crystallinity. Samples of both compounds showed a marked preferred orientation, due to the needle-like shape of the crystallites. In a sample from one well-crystallized batch of the tetrahydrate the effect was so strong that only the *hk*0-reflections had measurable intensities. The orientation was eliminated by suspending the powders in a concentrated starch gel. The dihydrate was then dried at 90°C, the tetrahydrate at room temperature. After a few trials samples could be prepared which no longer showed any evidence of a preferred orientation.

The diagram of $UO_4 \cdot 2H_2O$ was indexed by ZACHARIASEN[4] who found that this substance is orthorhombic with cell dimensions $a = 6.50 \pm 0.03$, $b = 4.21 \pm 0.02$, $c = 8.74 \pm 0.05$ Å, the uranium positions being (000), $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$. The complete pattern has also been published.[5]

The experimental data obtained in the course of the present investigation have been established to a greater degree of accuracy with regard to intensities and cell dimensions. It hereby became clear that the latter were variable from one sample to another, whilst the poor resolution of the α_1-α_2 doublet indicates that even within one sample the cell dimensions are not well defined. A correlation with the water content, which is also variable, could not be ascertained.

For the pattern listed in Table 1 the following cell dimensions were used for the calculation of $\sin^2 \theta$:

$$a = 6.502, \quad b = 4.216, \quad c = 8.778\ \text{Å}$$

For six different samples the cell dimensions were calculated, resulting in the following mean values:

$$a = 6.50 \pm 0.02, \quad b = 4.211 \pm 0.005, \quad c = 8.78 \pm 0.01\ \text{Å}$$

The cell volume is 240 ± 1 Å^3; the cell contains two formula units. The symmetry is orthorhombic body centred, the space group is probably I *mmm*.

The pattern of the compound $UO_4 \cdot 4H_2O$ has been published previously by DUNN[6] who, however, erroneously regarded it to be the dihydrate. At first sight the stronger reflections of the pattern showed hexagonal symmetry with $a = 6.8$ Å. It evolved, however, that these reflections are all doublets or triplets. The real symmetry, being only pseudo-hexagonal, proved to be base centered monoclinic.

For the tetrahydrate the same variability in cell dimensions and poor resolution of the α_1-α_2 doublet were observed as for the dihydrate.

For the pattern listed in Table 2 $\sin^2 \theta$-values were calculated with the following cell dimensions:

$$a = 11.85, \quad b = 6.785, \quad c = 4.245\ \text{Å}, \quad \beta = 93°37'$$

---

[1] T. SATO, *Naturwissenschaften* **48**, 668, 693 (1961).

[2] E. H. P. CORDFUNKE and A. A. VAN DER GIESSEN, *J. Inorg. Nucl. Chem.*, **25**, 553 (1963).

[3] E. H. P. CORDFUNKE and P. ALING, *Rec. Trav. Chim.* (1963) in press.

[4] W. H. ZACHARIASEN, CK 1367 (1944).

[5] R. UKAZI, *J. Atom. Engy Soc. Japan* **1**, 405 (1959).

[6] H. W. DUNN, ORNL 2092 (1956).

TABLE 1.—DIFFRACTION PATTERN OF $UO_4 \cdot 2H_2O$. CuKα-RADIATION, λ = 1.5418 Å

$\sin^2\theta \times 10^4$ obs	$\sin^2\theta \times 10^4$ calc	*hkl*	*I*	$\sin^2\theta \times 10^4$ obs	$\sin^2\theta \times 10^4$ calc	*hkl*	*I*	$\sin^2\theta \times 10^4$ obs	$\sin^2\theta \times 10^4$ calc	*hkl*	*I*
217.6	218.0	101	100	1602.4	1602.0	310	8	2684	2684.3	321	5
308.7	309.0	002	33	1649.6	1649.1	022	5	2781	2780.8	006	1
412.5	412.3	011	33	1711.5	1711.7	114	13	2828	2829.2	215	3
476.1	475.8	110	34	1798.6	1799.0	204	4	2838	2837.9	314	4
563.4	563.1	200	15	1903.3	1903.2	220	6	3139	3139.1	224	3
785.1	784.8	112	21	1911.4	1911.0	312	8	3155	3156.1	130	2
835.8	836.0	103	21	1961.6	1962.2	303	3	3257	3256.6	116	3
872.0	872.1	202	9	2072	2071.8	105	2	3284	3282.6	413	5
975.3	975.4	211	19	2177	2176.1	123	6		3295.3	323	
1029.8	1030.2	013	15	2211	2212.2	222	5	3413	3412.0	125	2
1235.5	1235.9	004	5	2252	2252.4	400	2	3465	3465.1	132	3
1341.8	1340.1	020	12	2270	2266.1	015	3	3487	3488.3	404	2
	1344.2	301		2557	2561.4	402	2	3595	3596.6	501	3
1558.2	1558.2	121	13	2576	2576.0	024	2		3592.5	420	
1592.8	1593.3	213	13	2664	2664.7	411	6	3654	3655.6	231	3
								3710	3710.5	033	1

TABLE 2 —DIFFRACTION PATTERN OF UO_4 $4H_2O$, CuKα RADIATION, λ = 1 5418 Å

$\sin^2\theta$ 10^4 obs	$\sin^2\theta$ 10^4 calc	*hkl*	*I*	$\sin^2\theta$ 10^4 obs	$\sin^2\theta$ 10^4 calc	*hkl*	*I*	$\sin^2\theta$ 10^4 obs	$\sin^2\theta$ 10^4 calc	*hkl*	*I*
171 5	170 0	200	100	1447 4	1447 9	$51\bar{1}$	6	2125	2124 0	402	1
	171 9	110		1466 9	1465 9	$11\bar{2}$	11	2213	2211 9	710	1
331 0	331 0	001	12		1468 6	$42\bar{1}$		2228	2227 1	530	2
471 2	471 0	$20\bar{1}$	10	1525 7	1523 1	$13\bar{1}$	10	2243	2240 4	240	1
488 6	487 9	$11\bar{1}$	19		1525 9	112		2289	2288 6	$62\bar{1}$	1
512 6	511 9	310	21		1530 0	600		2364	2365 9	$51\bar{2}$	2
517 6	517 6	020	32	1551 3	1547 1	330	10	2402	2401 4	041	3
	517 9	111			1553 1	131			2401 6	$42\bar{2}$	
532 0	531 0	201	5		1554 0	202		2439	2437 9	$71\bar{1}$	1
681 0	680 0	400	5	1593 2	1588 6	421	8	2467	2468 6	621	1
687 0	687 6	220	8		1597 9	511		2485	2483 1	$53\bar{1}$	1
798 3	797 9	$31\bar{1}$	5	1746 2	1745 9	$31\bar{2}$	2	2500	2501 1	$13\bar{2}$	1
848 0	848 6	021	7	1770 7	1771 0	$60\bar{1}$	1	2540	2541 4	$24\bar{1}$	1
887 1	887 9	311	6	1837 6	1833 1	$33\bar{1}$	5	2560	2561 1	132	1
951 7	951 0	$40\bar{1}$	5		1841 6	022		2602	2601 4	241	2
988 5	988 6	$22\bar{1}$	6	1923 7	1923 1	331	5	2630	2633 1	531	1
1049 0	1048 6	221	5		1925 1	312		2643	2641 6	422	2
1070 3	1071 0	401	5	1951 0	1951 0	601	4		2647 9	711	
1190 9	1191 9	510	5		1951 6	$22\bar{2}$		2665	2665 9	512	1
1197 2	1197 6	420	5	2048	2047 6	620	2	2720	2720 0	800	1
1207 6	1207 1	130	4	2070	2070 4	040	4	2752	2750 4	440	1
1324 3	1324 0	002	4		2071 6	222		2780	2781 1	$33\bar{2}$	1

Measurements on seven different samples resulted in the following mean values.

$$a = 11.86 \pm 0.02,\ b = 6.78 \pm 0.01,\ c = 4.245 \pm 0.004\ \text{Å},\ \beta = 93^\circ 28' \pm 10'$$

The cell volume is 341 ± 1 Å^3; the cell contains two formula units. The space group is C2, Cm or C2/m.

The structures of these two hydrates will be studied by neutron diffraction.

Acknowledgement—The author wishes to thank Dr. F. H. P. Cordfunke for suggesting the problem.

Reactor Centrum Nederland
Petten, The Netherlands

P. C. Debets

Extraction of thallium (III) from hydrochloric acid solutions

(*Received* 15 *November* 1962)

Irving[1] and Horrocks *et al.*[2] have studied the extraction of thallium (III) from hydrochloric acid solutions into ether and isopropyl ether. In the latter work, the form of thallium (III) extracted into the organic phase was postulated to be HTlCl$_4$. In an earlier investigation Benoit[3] had suggested the formation of several chloride complexes *viz.*, TlCl^{+2}, TlCl$_2^{+}$ and TlCl$_4^{-}$ in aqueous solutions. From this it would appear that in hydrochloric acid solution of thallium (III), a dynamic equilibrium exists between the species Tl^{+3}, TlCl^{+2}, TlCl$_2^{+}$, TlCl$_3$ and TlCl$_4^{-}$. The present study on the extraction behaviour of thallium (III) by tributyl phosphate (TBP) and trinonylamine (TNA) from aqueous solutions confirms the existence of TlCl$_4^{-}$. The extraction mechanism of TBP is fairly well-known. Trinonylamine, in the form of its chloride, functions as an anion exchanger. Recent work[4,5] using long chain amines as liquid ion exchangers shows that the charge on the anionic species can be inferred from such studies.

Thallium (III) chloride solution tagged with Tl-204 was prepared after Horrocks and Voigt.[2] It was purified by repeated precipitation of Tl(OH)$_3$, followed by dissolution in 6.5N hydrochloric acid. The thallium concentration was determined by the method of Kleinberg.[6] Pure benzene was used as diluent for the extractants.

In the solvent extraction studies, in each experiment the organic phase was pre-equilibrated with an aqueous phase having the desired hydrochloric acid concentration. This solvent phase was then equilibrated for 5 min with the aqueous solution of thallium (III) containing the same concentration of free hydrochloric acid. Ten fractions of both the phases were plated and the amount of thallium determined by counting the Tl-204 (β^- 0.76 MeV) using a G-M end-window counter.

The results using tributyl phosphate as the extracting agent are presented in Figs. 1 and 2. At constant concentrations of TBP (5%) and Tl (III) (0.93 × 10^{-4}M), the plot of log q (where q is the distribution ratio) against log c_{HCl} gives a slope of 2.7 (Fig. 1). At two fixed hydrochloric acid concentrations (1.6 and 6.3M), the plots of log q against log percent TBP show a slope of about 3 (Fig. 2).

The data using trinonylamine in benzene as the organic phase is presented in Fig. 3. At 0.1M hydrochloric acid concentration, the slope of the plot of log q against log percent TNA, is 1.1. For the HCl solution, 1.0M NaClO$_4$ has been added in order to reduce the distribution ratio so as to permit its determination more accurately. For this concentration also the slope is nearly unity (0.9). These results thus conclusively show that the thallium complex extracted is uninegatively charged and hence the species present is TlCl$_4^{-}$. In the concentration range studied no evidence for the existence of TlCl$_5^{-2}$ was obtained.

[1] H. M. Irving, *Quart. Rev.* **5**, 200 (1951).

[2] D. L. Horrocks and A. F. Voigt, *J. Amer. Chem. Soc.*, **79**, 2440 (1957).

[3] R. Benoit, *Bull. Soc. Chim. France*, 518 (1949).

[4] J. A. Brothers, R. G. Hart and W. G. Mathers, *J. Inorg. Nucl. Chem.*, **7**, 85 (1958).

[5] J. M. White, P. Kelly and N. C. Li, *J. Inorg. Nucl. Chem.*, **16**, 337 (1961).

[6] J. Kleinberg, *Collected Radiochemical Procedures* U.S. AEC Document, LA-1721, Los Alamos Scientific Laboratory, 1954.

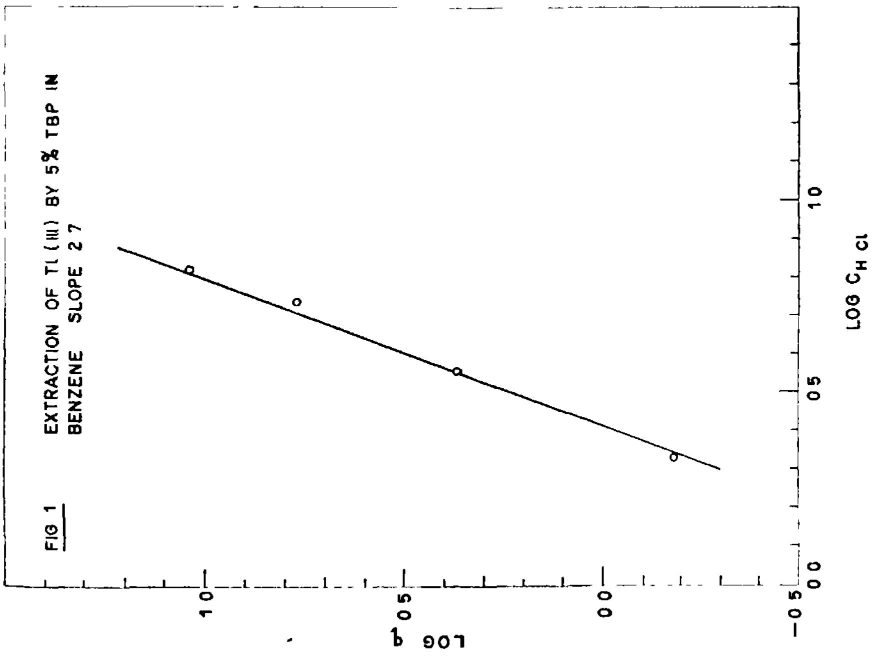


FIG 1
EXTRACTION OF Tl (III) BY 5% TBP IN BENZENE
SLOPE 2 7
LOG q
1 0
0 5
0 0
−0 5
0 0
0 5
1 0
LOG C_H Cl

Fig 1

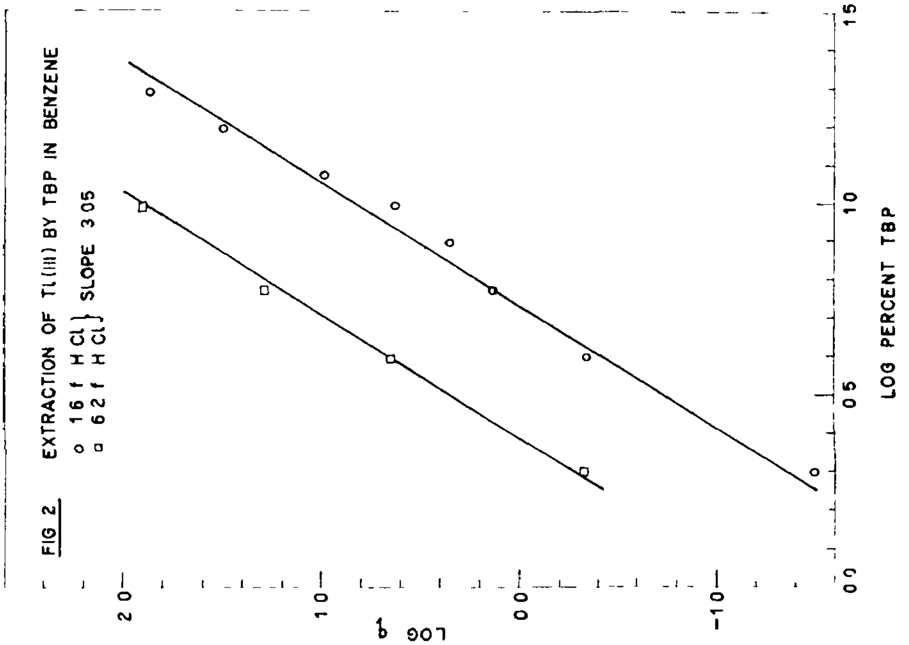


FIG 2
EXTRACTION OF Tl(III) BY TBP IN BENZENE
○ 1 6 f H Cl } SLOPE 3 05
□ 6 2 f H Cl
LOG q
2 0
1 0
0 0
−1 0
0 0
0 5
1 0
1 5
LOG PERCENT TBP

Fig 2

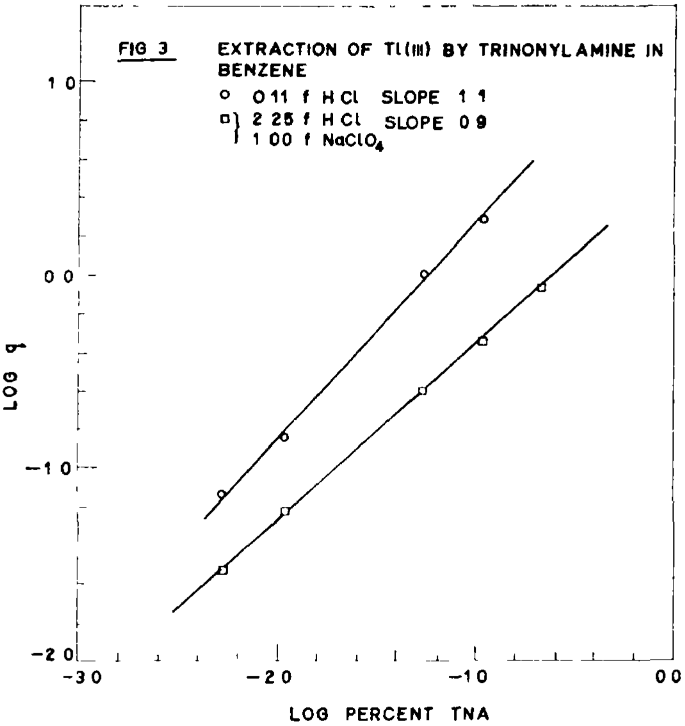


Fig 3

In the light of these results, the experimental data with tri n-butyl phosphate can also be interpreted The slope of nearly 3, obtained by varying the molarity of HCl at constant TBP concentration, might be explained by the conversion $TlCl_2^+ + H^+ + 2Cl^- \rightarrow HTlCl_4$ Acids such as $HTlCl_4$ will be extracted into TBP as ion pairs and will have a solvation number of 3 This perhaps explains the slope of 3 obtained in those experiments in which the TBP concentration was varied

Acknowledgement—The authors would like to express their sincere thanks to Dr J Shankar for his kind encouragement They would also like to thank Shri T K S Murthy for discussions

K S Venkateswarlu
P Charan Das

Uber die von Rice, Daasch, Holden und Kohn(1) beschriebenen Phosphornitrid-Chloridbromide

(*Received* 23 *January* 1963)

Zur Vervollstandigung von spektroskopischen Untersuchungen an den Phosphornitridhalogeniden(2), die in wichtigen Einzelheiten gegenuber Chapman und Paddock(3) abweichende Ergebnisse gebracht haben, stellten wir "$P_3N_3Cl_5Br$", "$P_3N_3Cl_4Br_2$" und "$P_3N_3Cl_2Br_4$" nach Rice *et al*(1) dar Wahrend $P_3N_3Cl_5Br$ auch nach unserer Ansicht eine einheitliche Verbindung ist, sind die weiteren Produkte Gemische

---

(1) R G Rice, L W Daasch, J R Holden, E J Kohn, *J Inorg Nucl Chem* **5**, 190 (1958)
(2) E Steger u R Stahlberg, *Z Naturforsch* **17b**, 780 (1962)
(3) A C Chapman, N L Paddock, *J Chem Soc* 635 (1962)

Wir mussen das zunachst aus den von uns beobachteten Schmelzpunkten und ihrer Veranderung bei weiterer Umkristallisation schliessen Die Verbindung "$P_3N_3Cl_4Br_2$" nach(1), Smp "132–134 C" oder "136°C" konnte auf einen Smp von 142°C gebracht werden Mit einem Smp 136°C wurde auch einmal ein Produkt aus einem Ansatz fur $P_3N_3Cl_5Br$ erhalten "$P_3N_3Cl_2Br_4$", Smp "167 169°C" nach(1), zeigt nach haufiger Umkristallisation aus Benzol Smp 176 177°C Besonders in Erscheinung tritt daneben eine Fraktion mit Smp 143 145°C

Unsere Infrarotspektren zeigen durch ihre Veranderungen beim Umkristallisieren der Substanzen ebenfalls deutlich den Mischungscharakter an und geben daruber hinaus Hinweise auf die Natur der Komponenten Fur "$P_3N_3Cl_4Br_2$" nach(1) folgt aus den zuruckgehenden Banden, besonders 604, 527, 492 cm^{-1}, dass $P_3N_3Cl_5Br$ mit vorliegt Kompensationsversuche mit Losungen dieses Stoffes im Vergleichsstrahlengang (IR-Spektralphotometer UR 10 aus Jena) zeigen an, dass er bei Smp 142 C 25%, danach bei 136 C 50% ausmacht Die Analyse von RICE *et al* (1) bedeutete dann, dass $P_3N_3BrCl_5$ + $P_3N_3Br_3Cl_3$ (1 1) erhalten worden war

$P_3N_3Br_3Cl_3$ ist auch, wie schwacher werdende Banden bei 507 und 595 cm^{-1} z B zeigen, ein Nebenbestandteil von "$P_3N_3Cl_2Br_4$", und zwar noch bei Smp 176 177 C Dieses enthalt auch noch die mit Smp 143 145 C angereicherte Substanz, bei der eine Absorption bei 1282 cm^{-1} auf tetrameres Phosphornitridhalogenid schliessen lasst Auf alle Falle ist "$P_3N_3Cl_2Br_4$" nach Rice *et al* ein komplizierteres Gemisch

Anmerkung bei der Korrektur (20 *March* 1963) Nach weiteren Versuchen ist "$P_3N_3Cl_5Br$" nicht einheitlich Von den "$P_3N_3Cl_5Br$" Substanzen (Smp 124 126 C) wurden bei "$P_3N_3Cl_4Br_2$" 2 Fraktionen (138 140 C, ohne Bande 529 cm^{-1}, 158 C, desgl ohne 600 cm^{-1}, $P_3N_3Cl_3Br_3$?) getrennt "$P_3N_3Cl_2Br_4$" enthalt auch $P_3N_3Br_6$

L STEGER
J ROST

Institut fur anorganische und
anorganisch-technische Chemie
Technische Universitat, Dresden

Separation of pure ^{90}Y from a ^{90}Sr-^{90}Y mixture by co-precipitation with ferric hydroxide

(*Received* 27 *December* 1962, *in revised form* 7 *February* 1963)

CO-PRECIPITATION with ferric hydroxide has been used as a standard method for separations in radio chemistry However, because of the poor separation, repeated precipitations are necessary, making the operation rather complicated The purity of ^{90}Y separated by co-precipitation with ferric hydroxide is especially inferior to that separated by other methods such as ion exchange and solvent extraction(1), and the poor separation may be due to the strong adsorptive power of gelatinous hydrated ferric hydroxide

Recently, the author observed on titrating pyridine(2) that cohesive and clean ferric hydroxide was precipitated from a ferric chloride solution This suggests that pyridine may be used to overcome the difficulties arising from the gelatinous precipitation, and an attempt was made to obtain a high degree of separation of ^{90}Y from a ^{90}Sr-^{90}Y mixture based on this observation

About 10^7 counts/min of a carrier-free ^{90}Sr-^{90}Y mixture was taken in a 50 ml beaker, and a $FeCl_3$ solution containing 1 mg of Fe^{3+} was added For the sake of comparison, ^{90}Y was first precipitated with dilute ammonia water Without adding both K_2SO_4 and $SrCl_2$ as carrier, almost all the ^{90}Sr and ^{90}Y was co-precipitated and the decay curve soon reached a stationary state In this case the degree of contamination of ^{90}Sr was $7\,2 \times 10^{-1}$ (Curve 1 in Fig 1) When 2% of K_2SO_4 was added, separation of ^{90}Sr and ^{90}Y took place and the degree of contamination of ^{90}Sr decreased to about one tenth of that previously ($8\,6 \times 10^{-2}$, Curve 2) Addition of 1 mg of Sr^{2+} reduced the degree of contamination further ($3\,7 \times 10^{-2}$, Curve 3), and the least degree of contamination of ^{90}Sr was obtained by adding both K_2SO_4 and $SrCl_2$ ($2\,0 \times 10^{-2}$, Curve 4)

(1) Y KODA, S MATSUO, H KIMURA, M YOSHIMOTO, K TANAKA, S ENOMOTO Reports of the Government Industrial Research Institute, Nagoya, **8**, 30, (1958)

(2) F P TREADWELL, W T HALL, *Analytical Chemistry*, Vol II, 9th Edition, p 495, Wiley New York (1942)

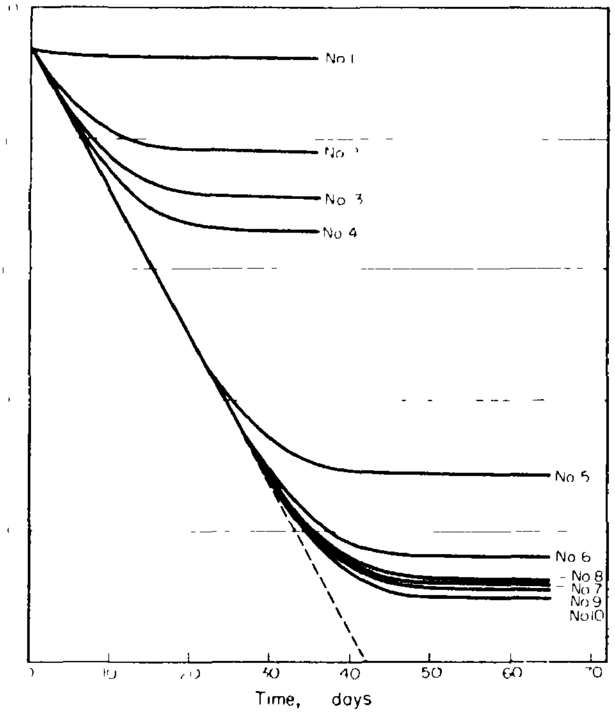


FIG. 1

When pyridine was used as a precipitant a low degree of contamination of the order of 10^{-4} was easily obtained even without adding K_2SO_4 and a carrier for ^{90}Sr (2.7×10^{-4}, Curve 5). In this case the precipitate was formed at a higher rate than in the case of ammonia water. When 0.1 ~ 5% of K_2SO_4 was added the degree of contamination decreased further as the concentration of K_2SO_4 was increased, reaching a value of ~10^{-5} (0.1% K_2SO_4, 6.3×10^{-5}, Curve 6, 1% K_2SO_4, 3.8×10^{-5}, Curve 7, 2% K_2SO_4, 4.2×10^{-5}, Curve 8, 5% K_2SO_4, 3.7×10^{-5}, Curve 9). The lowest degree of contamination was obtained by adding $SrCl_2$ simultaneously, and was 3.2×10^{-6} for 2% K_2SO_4 and 0.2 mg Sr^{2+} (Curve 10).

It seems that ferric hydroxide is the principal cause of the above phenomenon, which may be related to the fact that pyridine and SO_4^{2-} ions decrease the OH^- ion concentration in the solution as well as the degree of hydration of ferric hydroxide, which are accompanied by a remarkable decrease in the absorption of ^{90}Sr.

YOSHIO KODA

Government Industrial Research Institute
Nagoya
Hirate-machi Kita-ku Nagoya, Japan

A spectrophotometric investigation of the synergic solvent extraction system uranyl ion/tri-(n-octyl) phosphine oxide (TOPO)/di(2-ethylhexyl) phosphoric acid (D2EHPA)

(*Received* 25 *January* 1963)

FOR THE system uranyl ion/tri(n-octyl) phosphine oxide (TOPO)/excess di(2-ethylhexyl)phosphoric acid (D2EHPA) in kerosene the ratio TOPO : U in the complex formed has been investigated spectrophotometrically using the method of continuous variations. The principles of this method have been described in detail for instance by VOSBURGH and COOPER(1).

(1) W. C. VOSBURGH, G. R. COOPER, *J. Amer. Chem. Soc.*, **63**, 437 (1941).

Three mechanisms are considered for the formation of the UO_2^{2+}/D2EHPA/TOPO complex responsible for the high uranium distribution coefficient in a solvent extraction system consisting of a sulphuric acid aqueous phase and an organic phase containing kerosene, D2EHPA and TOPO These are as follows, where the particular reaction is given first, followed by its representation in general symbols

I $UO_2(X_2)(HX)_2 + n\,R_3PO \longrightarrow UO_2(X_2)(HX)_2(R_3PO)_n$
$AC_2 + n\,B \longleftrightarrow AC_2B_n$
(BLAKE *et al* [2], $n = 1$)

II $UO_2(X_2)(HX)_2(H_2O)_m$
$+ n\,R_3PO \longleftrightarrow UO_2(X_2)(HX)_2(H_2O)_{(m-n)}(R_3PO)_n + n\,H_2O$
$AC_2W_m + n\,B \longleftrightarrow AC_2W_{(m-n)}B_n + n\,W$
(IRVING and EDGINTON[3], $n = 1$)

III $UO_2(X_2)(HX)_2$
$+ n\,R_3PO \longleftrightarrow UO_2(X_2)(HX)_{(2-n)}(R_3PO)_n + n/2\,(HX)_2$
$AC_2 + n\,B \longleftrightarrow AC_{(2-n/2)}B_n + n/2\,C$
(KENNEDY,[1,5] $n = 1$ *or* 2)

For all three mechanisms the following side reactions must be taken into account[2]

$$\text{(a)}\quad B + C \longleftrightarrow BC,\ \frac{c_5}{c_2\cdot c_4} = K_a = 100 \pm 50$$

$$\text{(b)}\quad B + 1/2\ C \longleftrightarrow BC_{1/2},\ \frac{c_6}{c_2\cdot {c_4}^{1/2}} = K_b = 30 \pm 5$$

C is written for X_2, the dimeric D2EHPA anion, as well as for $(HX)_2$, the undissociated dimeric D2EHPA, for sake of simplicity The equilibrium concentrations of the components B, C, BC, $BC_{1/2}$ and W are designated as c_2, c_4, c_5, c_6 and c_7 The symbol for the equilibrium concentration of the (A + C) complex is c_1 that for the (A + C + B) complex is c_3

We have demonstrated for all three types of reaction, considering in every case both side reactions, that the method of continuous variations is suitable for the determination of the ratio TOPO : U (= n) in the UO_2/D2EHPA/TOPO complex Similar to the calculations of VOSBURGH and COOPER[1] we have derived formulae $n = f(x_m)$ for the three cases to be considered here[6] The following symbols and relations are used

x = volume fraction of primary solution B (TOPO) in the mixture
$1 - x$ = volume fraction of primary solution A (U) in the mixture
D = extinction of the mixture after the reaction has reached equilibrium
$\sum_1^i d_i$ = sum of the extinctions of the components before the reaction has taken place
$Y = D - \sum_1^i d_i$
x_m = x-value for the maximum (or the minimum respectively) of Y

It is found that the simple formula

$$n = x_m/(1 - x_m) \tag{1}$$

is valid if the component C is present in so great an excess as to allow the amount of C formed or consumed by the reactions to be neglected If a change in the concentration of C caused by the reactions has to be taken into account $n = f(x_m)$ takes the following form

$$n = \frac{x_m}{1 - x_m} + \frac{4c_2c_5 + c_2c_6 + c_5c_6 + (4c_5 + 3c_6)(c_3 - c_5 - c_6)}{M(1 - x_m)(4c_1 - 4c_5 - 3c_6)} \tag{2}$$

---

[2] C A BLAKE Jr *et al*, *Proc 2nd Geneva Conf* **28**, 289 (1958)

[3] H IRVING, D N EDGINTON, *J Inorg Nucl Chem*, **15**, 158 (1960)

[4] J KENNEDY, AERE-C/M-369 (1958)

[5] J KENNEDY, A M DEANE, *J Inorg Nucl Chem*, **19**, 142 (1961)

[6] H IHLE *et al*, Report Jul-74-PC (1962)

for reaction type (I) including side reactions (a) and (b)

$$n = \frac{x_m}{1 - x_m} - \frac{4c_2c_5 + c_2c_8 + c_3c_6 - (4c_2 + 6c_5 + 6c_8)(c_2 + c_5 + c_6)}{M(1 - x_m)(4c_1 - 4c_3 - 6c_5 - 6c_6)} \tag{3}$$

for reaction type (III) including side reactions (a) and (b). M is the concentration of the primary solutions in moles/l.

The equations (1), (2) and (3) have been derived for the condition that all mixtures for the complete set of continuous variation experiments are prepared with the same initial concentration of C and that the extinction coefficients of the components B, C, BC, $BC_{1/2}$ and W can be neglected.

The treatment of reaction (II) yields the same result as that for type (I) (i.e. eqn. (2)) provided that the amount of free water present in the solutions before reaction (II) takes place is negligible compared with that set free in reaction (II).

Using equations (2) and (3) together with expressions for limiting values of c_1, c_2 etc. derived from the equations for these concentrations it is possible to calculate upper limits for the second term in equations (2) and (3), giving the deviation of n from the experimentally determined value of $x_m/(1 - x_m)$ for a given initial concentration of C. A lower limit for the concentration of C can thus be derived for a set of experiments to which equation (1) applies. An additional set of equations connecting n, the concentration c_3, and the dissociation constant K_d of the UO_2/D2EHPA/TOPO-complex in an implicit form can be derived by the method of HAGENMULLER[7, 8]. These equations can be applied to determine limiting values for c_3 and K_d and they supply additional information limiting the necessary initial concentration in C to lower values than those set by the above mentioned expressions alone.

Experiments and results

Measurements were made between 4500 and 3900 Å with a Cary No. 14 spectrophotometer. Because of the small difference in absorption between the UO_2^{2+}/D2EHPA-complex and the UO_2^{2+}/D2EHPA/TOPO complex the absorption of each (UO_2^{2+} + D2EHPA + TOPO) solution was measured against a reference solution containing the same concentration of UO_2^{2+} and of D2EHPA, a correction being applied for the very slight absorption of the TOPO. The solutions were 10^{-3} to 10^{-2} *M* in uranium and TOPO and a large excess of D2EHPA (0.1 *M*) secured that the sole UO_2/D2EHPA-complex (containing no TOPO) present in the solutions was the $UO_2X_2(HX)_2$[2].

Curves of $Y = f(x)$ at several different wave lengths λ all reach their maximum or minimum at $x_m = 0.5 \pm 0.02$, and the curves $Y = f(\lambda)$ pass through zero at several different λ-values that are independent of x. These results are only possible if in the concentration range investigated there is only one complex U/D2EHPA/TOPO or if all existing complexes U/D2EHPA/n TOPO have the same molar extinction coefficient as the one with $n = 1$[1].

It follows from $x = 0.5$ that we have proved the existence of a complex with a TOPO : U ratio of $n = 1$ in the concentration range investigated, since the formation of polynuclear complexes is excluded by the results of BAES *et al.*[9] By the methods outlined above the maximum deviation of n from the value $x_m/(1 - x_m)$ can be calculated to be 4% under our experimental conditions. Upper limits for the dissociation constant K_d of the U/D2EHPA/TOPO complex can be calculated from the upper limits for c_1 and c_2 together with lower limits for c_3 and c_4. For the different mechanisms considered we have obtained the following results

Mechanism I $K_d \le 1.4 \times 10^{-3}$
Mechanism II $K_d \le 1.8 \times 10^{-2}$
Mechanism III $K_d \le 7.5 \times 10^{-4}$

Arbeitsgruppe
Physikalische Chemie der KFA Jülich e.V.
Im Institut für Physikalische Chemie der Universität Bonn
Bonn, Wegelerstr. 12

H. IHLE
H. MICHAEL
A. MURRENHOFF

---

[7] P. HAGENMULLER, *C.R. Acad. Sci. Paris*, **230**, 2190 (1950).
[8] H. L. SCHLÄFER, In *Komplexbildung in Lösung* p. 232. Springer, Berlin (1961).
[9] C. F. BAES *et al.*, *J. Phys. Chem.*, **62**, 129 (1958).

Preparation of technetium metal

(*Received* 14 *February* 1963)

TECHNETIUM metal has been prepared in bulk by reduction of the heptasulphide or of ammonium pertechnetate with hydrogen gas.(1) It has also been reported that technetium at tracer level can be electrodeposited from baths of 2N sulphuric acid containing a trace of fluoride.(2) We have prepared technetium metal in bulk by electrodeposition, and also by decomposition of ammonium hexachlorotechnetate.

Films of technetium metal 5 mg/cm^2 thick have been electrodeposited on to copper, using a plating bath of 0.2% technetium as ammonium pertechnetate in 2N sulphuric acid, and a platinum anode. The current density was in the range 25-30 mA/cm^2. Agitation was by means of a circulating pump, giving a flow rate of 50 ft/min across the electrodes, and the bath was initially at room temperature, rising during the process to about 40°C. We have found that on our scale of operation the addition of small quantities of fluoride (N/100), to the bath does not affect the process in any way.

The technetium plates as a bright silver deposit, but deposition stops after about a quarter of the total technetium has been deposited. This is due to the accumulation of a brown compound of technetium, formed by reduction of ammonium pertechnetate, in the bath. We have established that this brown compound does not move under paper electrophoresis, and contains 4-valent technetium.

Complete deposition of the technetium may be obtained by the continuous addition of small quantities of hydrogen peroxide just sufficient to oxidize the brown compound back to pertechnetate as the process continues.

It is of interest to note that reduction at a mercury cathode gives a technetium amalgam, and under these conditions 100% of the technetium can be deposited, although the brown compound is observed in the solution.

We have also prepared technetium metal, as mentioned above, by heating ammonium hexachlorotechnetate $[(NH_4)_2TcCl_6]$ in an inert atmosphere, e.g. nitrogen, at a dull red heat. The salt does not melt but decomposes under these conditions to leave technetium metal as a fine silver-grey powder. We have found that rhenium metal may be prepared in a similar way, from ammonium hexachlororhenate.

J. D. EAKINS
D. G. HUMPHRIES

A.E.R.E., Harwell
Didcot, Berks.

(1) J. W. COBBLE, C. M. NELSON, G. W. PARKER, W. T. SMITH, Jr., G. E. BOYD, *J. Amer. Chem. Soc.* **74**, 1852 (1952).

(2) G. E. BOYD, *J. Chem. Educ.* **36**, 3 (1959).

Synthesis of anhydrous aluminium perchlorates

(*Received* 28 *December* 1962)

THE application of 2,2′-dimethoxypropane for the dehydration of hydrated inorganic salts, as well as for the synthesis of new coordination compounds of certain transition metal perchlorates, has been reported recently.(1,2)

Anhydrous aluminium perchlorate, a possible starting material for the preparation of aluminium perchlorate-amine complexes cannot be obtained by heating any of the known hydrates and the anhydrous perchlorate prepared by ACERETE and LACAL's method,(3) which cannot be used *in situ*,

(1) K. STARKE, *J. Inorg. Nucl. Chem.* **11**, 77 (1959) (incl. ref. cited therein).

(2) D. W. MEEK, R. S. DRAGO and T. S. PIPER, *Inorg. Chem.* **1**, 285 (1962).

(3) J. G. ACERETE and Y. R. U. LACAL, *Rev. Acad. Cienc. Zaragoza* (*Series* 2*A*), **9**, 117 (1954) (incl. ref. cited therein).

imposes the danger of handling this very shock sensitive material. Therefore, the reaction of $Al(ClO_4)_3 \cdot 9H_2O$ with 2,2′-dimethoxypropane was studied. It was found that the resulting reaction mixture can be used for the preparation of anhydrous aluminium perchlorate coordination compounds. The preparation of $Al(ClO_4)_3 \cdot 4$ pyridine is described to illustrate the utility of this procedure.

Experimental

All reactions and manipulations were carried out in an argon atmosphere. $Al(ClO_4)_3 \cdot 9H_2O$ (G. F. Smith Chem. Corp.), 2,2′-dimethoxypropane (b.p. 77°–82°), and pyridine (Matheson, Coleman and Bell) were used together with sodium-dried ether as a wash-liquid. The infrared spectra were obtained with a Perkin-Elmer Infracord Model 137 using standard KBr-pellet techniques. X-ray powder data were obtained with a Norelco X-Ray-Diffractometer (Cu-Target and Ni-Filter). A Cary spectrophotometer was used to obtain absorption spectra in the visible range.

When 2.4 g (0.005 mol.) of $Al(ClO_4)_3 \cdot 9H_2O$ was stirred with 25 ml of 2,2′-dimethoxypropane, the perchlorate dissolved in the acetal forming at first a yellow bottom layer and a colourless top layer. The dehydration proceeded with an increase in colouration (yellow-brown to brownish-red) of the bottom layer. Infrared samples taken at 10 min intervals showed that methanol, formed by the interaction of 2,2′-dimethoxypropane with the hydrate was exclusively in the bottom layer (containing the $Al(ClO_4)_3$ as a solvate). Acetone could be observed in both layers in equal amounts. After 3 hr the solution turned completely red-brown, the addition of 4 ml of pyridine decolourized the solution immediately, and a white precipitate formed. The compound was filtered, washed with ether, and dried under high vacuum. Anal. Calcd. for $Al(ClO_4)_3 \cdot 4$ Pyridine: Al, 4.2, Cl, 16.6, N, 8.72, C, 37.7, H, 3.1%. Found: Al, 4.1, 4.2, Cl, 17.1, 17.0, N, 8.71, C, 37.4, H, 3.0%. The infrared spectrum showed the following absorptions: 3420(vs), 3080(s), 2830(s), 2050(s), 1645(s), 1610(s), 1530(s), 1480(s), 1340(w), 1250(w), 1150(vs), 1600(vs), 944(w), 758(vs), 682(vs) [cm⁻¹].

An X-Ray powder photograph indicated a crystalline structure. The observed data are listed below.

2	15.82	20.51	21.75	24.14	26.01	31.87	33.3	44.5	46.31	48.74	52.60
d	5.6	4.31	4.08	3.68	3.42	2.80	2.69	2.04	1.96	1.87	1.74
I	M	VS	VVW	M	M	S	VVW	VVW	VVW	VVW	VVW

I: intensity estimated.

Discussion

The dehydration of $Al(ClO_4)_3 \cdot 9H_2O$ using the 2,2′-dimethoxypropane system represents an alternate route to the preparation of anhydrous aluminium perchlorate coordination compounds. As reported previously,[1] such dehydrations proceed through the formation of 2 moles of methanol and 1 mole of acetone per mole water. The colouration of the solution during the dehydration[4] possibly resulted from the presence of small amounts of $HClO_4$ which is known to produce coloured solutions by interaction with acetone. A solution made from 70% $HClO_4$ and acetone in a 1:5 volume ratio had a similar absorption spectrum as observed for the original reaction solution (434.5 mμ, 490.0 mμ). The presence of $HClO_4$ could be explained by a reaction such as

$$Al(ClO_4)_3 \cdot n(CH_3OH) \rightleftharpoons HClO_4 + Al(ClO_4)_2OCH_3 \cdot (n-1)(CH_3OH) \quad \text{I}$$

The addition of base could either consume the product on the left side of the equation or could neutralize the acid directly. After the addition of a small amount of pyridine the colour disappears and the white precipitate forms.

Debye-Scherrer Powder diagrams of the pyridine-aluminium perchlorate complex show a crystalline structure, possibly of tetragonal symmetry. The available infrared data are not very helpful in indicating the nature of the bonding between the pyridine and the aluminium cation. Studies on the structure of the pyridine complex and on coordination compounds of aluminium perchlorate with different ligands are under investigation and will be the subject of a further communication.

---

[4] Similar reactions with $Mg(ClO_4)_2 \cdot 6H_2O$ and $Li(ClO_4) \cdot 3H_2O$ remain colourlesss during the dehydration (unpublished observations).

Acknowledgement—The author wishes to thank Dr I S MacKenzie for helpful discussions and Mr H Frankel, Miss R Juurik and Mrs N Bolan for their assistance This work was supported by the Advanced Research Projects Agency (ARPA) under Contract No DA-30-069-ORD-2638

Research Laboratory, General Chemical Division
Allied Chemical Corporation
Morristown, New Jersey

G Franz

The thermogravimetric analysis of some complex oxalates

(*Received* 10 *February* 1963)

In the course of a study into the decomposition of a number of inorganic oxalates the thermogravimetric decomposition in air of chromium potassium oxalate $Cr_2(C_2O_4)_3$ $3K_2C_2O_4$ $5H_2O$, sodium chromium oxalate $Cr_2(C_2O_4)_3$ $3Na_2C_2O_4$ $5H_2O$ and potassium titanyl oxalate, TiO C_2O_4 $K_2C_2O_4$ - $2H_2O$ have been carried out

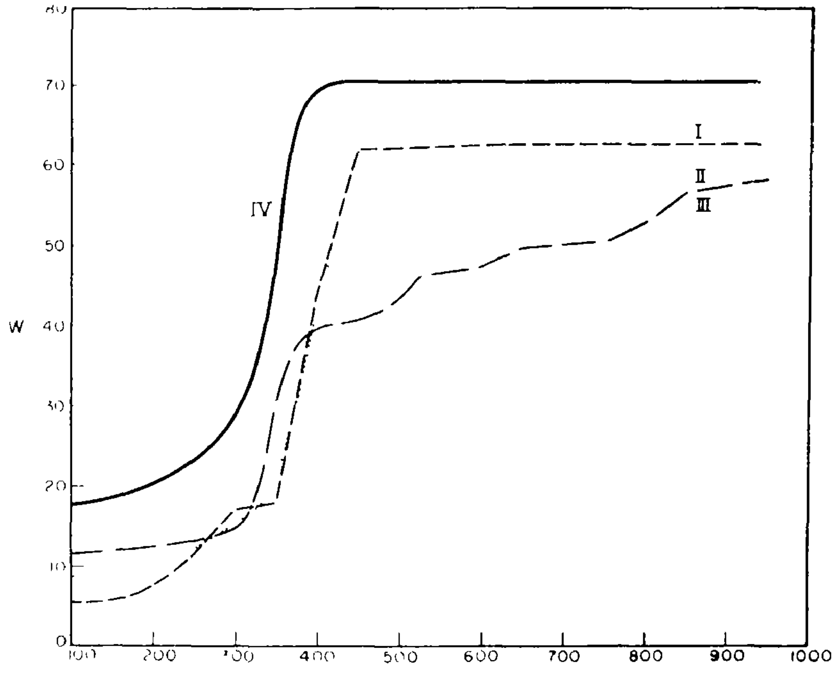


Fig 1 - Thermogravimetric decomposition of complex oxalates
I Chromium sodium oxalate
II Chromium potassium oxalate
III Titanyl potassium oxalate
IV Chromium oxalate

The apparatus used was an automatically recording decomposition balance in which the rate of heating was 6°/min The recorded traces were analysed and plotted as percentage weight lost (w) against temperature (T°C) (Fig 1) Each sample was first heated at 100 C until constant weight was attained, which accounted for the loss of some water in each case

The decomposition of the double salts of chromium can be compared with that of the corresponding simple oxalates The decomposition of chromium oxalate, $Cr_2(C_2O_4)_3$ $6H_2O$ proceeds directly to Cr_2O_3 without any intervening plateau corresponding to the anhydrous salt (see figure) and is complete at 400°C Sodium and potassium oxalates are very similar to each other in behaviour, the potassium salt being the less stable The decomposition temperatures are (a) $M_2C_2O_4 \rightarrow M_2CO_3$, 500 600 C (M - K), 550 600°C (M = Na), (b) $M_2CO_3 \rightarrow M_2O$, 800–900°C (M K), above 950°C (M Na)

These temperatures agree with those reported by AKALAN(1) for the first stage of this decomposition

The most plausible interpretation of curves I and II which can be undertaken at present rests on the assumption that water in excess of that in the formulae can be taken up, but is lost at 100°C

The extent of this deliquescence is quite considerable 5 3 water molecules having been adsorbed by the potassium salt and 2 8 by the sodium salt

The slow part of each decomposition up to about 300 C can be accounted for by the loss of more strongly combined water The theoretical values of *W* for the loss of the water of crystallization are 15 5 for the sodium salt and 19 0 for the potassium salt so that the first plateau on curve I does not occur until the compound has decomposed beyond the dehydration stage This is in contrast to the simpler oxalates (2) The next stage in the decomposition which is complete at 450 C for the sodium salt but finishes rather more slowly in the case of the potassium salt, continues until the most stable oxides of each metal remain ($3M_2O$, + Cr_2O_3) Theoretical values of *w* based on this assumption are *W*, 62 6 (M Na), and *w*, 59 4 (M K) Samples of the two double salts of chromium heated to between 900–950°C showed no trace of carbonate in the residue

TABLE I —STAGES IN THE DECOMPOSITION OF POTASSIUM TITANYL OXALATES

Experimental *w*	Temperature range (C)	Possible product	Theoretical *w*
11 5	100	$K_2TiO\ (C_2O_4)_2$	10 5
39 41	400 475	$K_2CO_3\ TiO_2$	38 5
46 5 47 5	525-600	$K_2O_2\ TiO_2$	46 5
50 5	650 750	$K_2O\ TiO_2$	50 5
55 5	850 900	$K_2O\ TiO$	54 5

Although a certain amount of instability is shown by both these products, this interpretation would be in accord with the notion of oxalate ions co-ordinated to a central chromium ion

The decomposition temperature is similar for each compound and higher than that of the simple chromium oxalate, and this is compatible with the expected stabilizing effect of complex formation Such an explanation is also supported by the absence of carbonate in the solid residue, as indicated by the chemical tests, or by calculations based either on the stoichiometric formula or the formula used in the interpretation of the results

In the case of the potassium titanyl oxalate no information regarding a simple titanyl oxalate could be obtained Attempts to prepare this salt by a method quoted in the literature(3) were not successful A comparison of the five experimental plateaux with possible products is made in Table 1

One of us (D N) wishes to thank the D S I R for a research grant

The Chemistry Dept
The Royal College of Advanced Technology
Salford, Lancs

D DOLLIMORE
D NICHOLSON

---

(1) S ALKALAN, *Rev Fac Sci, Univ Istanbul* **21C**, 184 (1956)
(2) J ROBIN, *Bull Soc Chim France*, 1078 (1953)
(3) P P BHATNAGER and T BANERJEE, *J Sci Ind Res* **15B**, 715 (1956)

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 741 to 744. Pergamon Press Ltd. Printed in Northern Ireland

LETTERS TO THE EDITORS

On the decay of ^{72}Zn

(*Received* 15 *November* 1962)

THE DECAY of ^{72}Zn was first investigated by SIEGEL and GLENDENIN.(1) They separated zinc from other fission products of ^{235}U and measured a half-life of 49 hr. By the aluminium absorption method they found a main β-component of 0.3 MeV energy and a possible β-component of low intensity and of about 1.6 MeV energy. A redetermination of the half-life by KJELBERG *et al.*(2) yielded a value of 46.5 hr. A 40 msec isomeric state of ^{72}Ga of 100 keV energy, studied by (n, γ) reaction on ^{71}Ga, is also known.(3)

The aim of this work was to gather new information on the β and γ-rays present in the decay of ^{72}Zn. While it was in progress, THWAITES(4) reported two γ-rays at 144 ± 2 keV and 193 ± 4 keV with an intensity ratio of 10:1; they did not appear to be in coincidence. He found no γ-rays which would account for the difference between the β-rays at 0.3 and 1.6 MeV. Besides these two γ-rays, other transitions of lower energy and intensity, including a 100 keV transition being probably the isomeric transition of ^{72m}Ga, were recently observed by HAGEBØ *et al.*(5)

In our work, ^{72}Zn was produced in thermal neutron fission of ^{235}U. Because of its very low fission yield, high initial activities were necessary: targets of about 200 mg of 90 per cent enriched ^{235}U were irradiated during 2 days in the BR1 reactor at Mol. The thermal neutron flux was of 4.5×10^{11} neutrons/cm^2 sec. The sample was allowed to cool for 1 day. The separation chemistry of zinc followed that of SIEGEL and GLENDENIN(1) based on precipitations of $ZnHg(SCN)_4$. Because of the high activity of the target, the initial step in the separation, dissolution of the uranium and the first precipitation of $ZnHg(SCN)_4$, was performed by remote control. Further purifications were necessary: passing the solution in HCl 6M on a Dowex 1 ion exchange column, from which the zinc was eluted with water, followed by extraction at pH 4–5 with dithizone and back-extraction in HNO_3 0.2 M. However in some experiments contamination by other fission products did still interfere (up to 10 per cent of the ^{72}Zn activity).

The γ-spectrum was measured with a 2 × 2 in NaI(Tl) crystal and recorded on a multichannel analyser. Peaks at 147 ± 2 keV and 194 ± 2 keV were observed. The intensity of the 194 keV peak was of 10 ± 0.5 per cent of the 147 keV peak. No coincidences between these γ-rays could be found using a fast-slow coincidence circuit of resolving time $2\tau = 2 \times 10^{-8}$ sec. No γ-rays of higher energy belonging to ^{72}Zn could be detected. These results confirm the work of THWAITES. Owing to the presence of contaminants, the γ-rays of lower energy and intensity seen by HAGEBØ *et al.*(5) were not evident in this work.

Before radiogenic growth of 14 h ^{72}Ga could interfere, the β-spectrum of freshly separated samples of ^{72}Zn was measured on a 2 in. × 0.5 in. windowless anthracene crystal and recorded on a 256 channel analyser in coincidence with the intense 147 keV γ-peak. The resolving time of the coincidence circuit was $2\tau = 2\ \mu$sec and the thickness of the sources was of the order of a few mg/cm^2. The Kurie plot showed a β-ray of 0.26 ± 0.02 MeV maximum energy. Among other standards the 0.26 MeV β-ray of ^{45}Ca was used.

---

(1) J. M. SIEGEL and L. E. GLENDENIN, paper 53 in *Radiochemical Studies: The Fission Products*, C. D. CORYELL and N. SUGARMAN (Editors) NNES Div. IV, 9. McGraw Hill, New York (1951).

(2) A. KJELBERG, H. TANIGUCHI and L. YAFFE, *Canad. J. Chem.* **39**, 635 (1961).

(3) F. C. CAMPBELL and P. F. FETTWEIS, *Nucl. Phys.* **13**, 92 (1959); K. F. ALEXANDER and V. BREDEL, *Nucl. Phys.* **17**, 153 (1960); P. F. FETTWEIS and E. C. CAMPBELL, *Nucl. Phys.* **33**, 272 (1962).

(4) T. T. THWAITES, *Bull. Amer. Phys. Soc.* ser. II, **7**, 341 (1962).

(5) A. KJELBERG, private communication; E. HAGEBØ, A. KJELBERG and R. NORDHAGEN, to be published.

Evidence seems conclusive that a 1.6 MeV β-component is absent in the decay of ^{72}Zn. Although extrapolation from the straight line joining the energy differences between the known Ga and Zn isobars of even mass, as given by WAY and WOOD⁽⁶⁾ would predict an energy difference of 1.5 MeV between ground states of ^{72}Zn and ^{72}Ga, while Cameron's mass formula⁽⁷⁾ shows a 1.14 MeV mass difference, the observed one is only of about 0.41 MeV.

The assignment of spins is puzzling. Although the low intensity γ-rays observed by HAGEBO *et al.* were not studied in this work, it is obvious that the main branching in the decay of the even-even nucleus ^{72}Zn passes through the 0.26 MeV β and the 147 MeV γ-transitions. The log ft value for the β-ray is close to 4.5 which is compatible with an allowed transition and indicates a 1⁺ or 0⁺ spin for a ^{72}Ga level at 147 keV. To reach the 3 spin of the ground state⁽⁹⁾ the latter should decay with an M2 or an E3 multipolarity. The theoretical reduced transition probabilities for such a transition are too small to be consistent with the β-γ coincidence measurement. Due to this discrepancy, no clear conclusions can be drawn from our work.

Acknowledgements—We wish to thank C. VAN DER VORST for the remote control operations, A. SPEECKE for some zinc purifications and J. COLARD for handling part of the counting. We are indebted to A. KJELBERG for communicating unpublished data on ^{72}Zn.

Centre d'Etude de l'Energie Nucléaire
Mol, Belgium

P. DEL MARMOL
P. FETTWEIS

⁽⁶⁾ K. WAY and M. WOOD *Phys. Rev.* **94**, 119 (1954).

⁽⁷⁾ A. G. W. CAMERON AECL report no 433 (1957).

⁽⁹⁾ Nuclear Data Sheets National Academy of Science, National Research Council, Washington, D.C. NRC-59-26.

Potassium pentachlorovanadium (III)

(*Received* 27 *October* 1961; *in revised form* 25 *February* 1963)

SEVERAL salts of the ion $[VCl_5H_2O]^{2-}$ were reported in 1904 by STAHLER⁽¹⁾. These were prepared by evaporation of solutions under an HCl atmosphere. He reported that thermal decomposition of these salts led to oxycompounds. The only other work on halide complexes of V(III) that has appeared in the literature is a study of fused salt systems by BECK⁽²⁾ which revealed the existence of $KVCl_4$.

We have prepared $K_2VCl_5 \cdot 4H_2O$ by a different route and have dehydrated it to stable K_2VCl_5. The hydrate was prepared by dissolving VCl_3 in concentrated 11.3 N HCl to give an 0.5 M solution. KCl was then added to give 1.0 M K^+. Care must be taken to maintain an inert atmosphere (e.g., Ar or N_2) by using a closed Pyrex^{R} vessel equipped with reagent inlet and outlet tubes and a sintered-glass disc for filtration in the absence of air. Hydrogen chloride was bubbled through the solution for 18 hr. During this time the mixture was cooled to −30 C. Green crystals of $K_2VCl_5 \cdot 4H_2O$ separated from solution and were washed with dioxane or CCl_4. The mother liquor might be more effectively removed with more polar organic solvents if it were not for their destructive effect on K_2VCl_5. The tetrahydrate is hygroscopic. When heated in Ar or N_2 to 100-125 C, this tetrahydrate readily loses all of its water to form violet K_2VCl_5.

Potassium pentachlorovanadium (III) is a pink hygroscopic crystalline solid. It is thermally stable in air to 270 C and in Ar to 400 C. The decomposition is complex with little VCl_4 being evolved and mixed valence states are found in the residues. A powder pattern was obtained for K_2VCl_5 using filtered Cu radiation and a Straumanis-type X-ray diffraction camera of 57.3 mm radius. The complex pattern obtained probably represents a monoclinic or triclinic structure. A structure similar to that of Tl_2AlF_5[3], where molecules share an anion to gain octahedral coordination in a chain structure, seems improbable from a comparison of patterns.

⁽¹⁾ A. STAHLER, *Ber.* **37**, 4411 (1904).

⁽²⁾ G. BECK, *Z. anorg. allgem. Chem.* **174**, 31 (1928).

⁽³⁾ C. BOSSET, *ibid.* **235**, 139–47 (1937).

The solubility of K_2VCl_5 in the common organic solvents, acetone, ether, dioxane, methanol and n-propanol, was moderate and proceeded by decomposition of the complex, giving a solution of VCl_3 and a precipitate of crystalline KCl. Chlorination of K_2VCl_5 by Cl_2 begins at 190°C, yielding VCl_4 vapours and a KCl residue.

The authors are indebted to Mrs Gloria Faulring for conducting the X-ray examination.

Union Carbide Metals Company

P. H. CRAYTON*
W. A. THOMPSON

* Present address: The Carborundum Company, Niagara Falls, New York.

The structure of some new mixed metal oxides containing lithium

(*Received* 18 *February* 1963)

IN THE course of an investigation on the crystal chemistry of compounds with spinel structure we prepared some new mixed metal oxides containing lithium, viz. $LiMg_{0.5}Ti_{1.5}O_4$, $LiCo_{0.5}Ti_{1.5}O_4$, $LiCu_{0.5}Ti_{1.5}O_4$ and $LiZn_{0.5}Ti_{1.5}O_4$, $LiMnTiO_4$ and $LiGaTiO_4$, $LiCrMnO_4$, $LiRhMnO_4$ and $Li_{4/3}Mn_{5/3}O_4$, all with spinel structure and $LiGaGeO_4$ with phenacite structure.

These compounds were prepared by heating an intimate mixture of high-purity oxides or carbonates for several hours at 950°C in an atmosphere consisting of an 80:20 mixture of oxygen and carbon dioxide. X-ray diagrams were obtained with a Philips X-ray diffractometer using CoKα or CuKα radiation. A survey of our results is given in Table 1. The following facts are noteworthy.

TABLE 1.—NEW MIXED METAL OXIDES CONTAINING LITHIUM

Formula	Structure	Lattice parameters (Å)		Cation distribution*
$LiMg_{0.5}Ti_{1.5}O_4$	spinel (with superstructure)	a	8.37	$\approx Li_{0.5}Mg_{0.5}[Li_{0.5}Ti_{1.5}]$
$LiCo_{0.5}Ti_{1.5}O_4$	spinel (with superstructure)	a	8.36	$\approx Li_{0.5}Co_{0.5}[Li_{0.5}Ti_{1.5}]$
$LiCu_{0.5}Ti_{1.5}O_4$	spinel	a	8.39	$\approx Li_{0.7}Cu_{0.3}[Li_{0.3}Cu_{0.2}Ti_{1.5}]$
$LiZn_{0.5}Ti_{1.5}O_4$	spinel (with superstructure)	a	8.37	$\approx Li_{0.5}Zn_{0.5}[Li_{0.5}Ti_{1.5}]$
$LiMnTiO_4$	spinel	a	8.30	$Li[Mn^{3+}Ti^{4+}]$
$LiGaTiO_4$	spinel	a	8.28	$Li_{0.5}Ga_{0.5}[Li_{0.5}Ga_{0.5}Ti]$
$LiGaGeO_4$	phenacite	a	13.90	
		c	9.29	
$LiCrMnO_4$	spinel	a	8.19	$Li[Cr^{3+}Mn^{4+}]$
$LiRhMnO_4$	spinel	a	8.30	$Li[Rh^{3+}Mn^{4+}]$
$Li_{4/3}Mn_{5/3}O_4$	spinel	a	8.19	$Li[Li_{1/3}Mn^{4+}_{5/3}]$

* octahedral site cations between brackets.

(a) The cation distribution of the spinels $LiMe^{2+}_{0.5}Ti_{1.5}O_4$ was calculated from the intensities of the X-ray reflections starting from the model $Li_{0.5+x}Me^{2+}_{0.5-x}[Li_{0.5-x}Me^{2+}_{x}Ti_{1.5}]O_4$ with ideal oxygen parameter ($u = 0.375$). For the compounds with Me = Mg, Co and Zn we found $0 \leq x \leq 0.1$, for the one with Me = Cu $x \approx 0.2$ (reliability index R about 13 per cent). Besides the spinel reflections we found the same superstructure reflections as have been found for ordered lithium ferrite $Fe[Li_{0.5}Fe_{1.5}]O_4$.[1] This means that in these titanates we have a 1:3 order of mainly Li^+ and Ti^{4+} ions on octahedral sites.

---

[1] P. B. BRAUN, *Nature* **170**, 1123 (1952).

The spinels $LiCo_{0.5}Ti_{1.5}O_4$ and $LiZn_{0.5}Ti_{1.5}O_4$ can be compared with those reported recently by DURIF and JOUBERT(2), viz. $LiCo_{0.5}Ge_{1.5}O_4$ and $LiZn_{0.5}Ge_{1.5}O_4$ with analogous cation distribution and superstructure. We believe that the occurrence of the tetravalent ions on the octahedral sites in these compounds is favoured by anion polarization(3), which is large for the distribution with these ions on octahedral sites.

We did not succeed in preparing $LiNi_{0.5}Ti_{1.5}O_4$.

(b) The cation distribution of the spinels $LiMe^{3+}Ti^{4+}O_4$ depends strongly on the nature of the Me^{3+} ion. All spinels of this type so far obtained have the Li^+ ions on tetrahedral sites, except $LiFeTiO_4$ (in which 0.5 Li^+ + 0.5 Fe^{3+} are on tetrahedral sites)(3) and $LiGaTiO_4$, for which from the intensities of the X-ray reflections we found approximately 0.3 Li^+ + 0.7 Ga^{3+} on tetrahedral sites.

The X-ray diagram of slowly cooled $LiGaTiO_4$ showed a number of weak superstructure lines which are indentical with those found for $LiZnSbO_4$(1). Probably there is a 1:1 order on the octahedral sites between the Li^+ and the Ti^{4+} ions, which is partly disturbed by the small amount of Ga^{3+} ions on these sites. A sample of $LiGaTiO_4$ quenched from 1000°C did not show any of these extra X-ray reflections.

(c) Since the Mn^{4+} ion is isoelectronic with the Cr^{3+} ion ($3d^3$) we expect it to have a marked preference for octahedral sites. This is confirmed by the cation distributions found experimentally. Since the X-ray reflections (220) and (422), to which only the tetrahedral site cations contribute, are absent, the tetrahedral sites are completely occupied by lithium ions, i.e. the Mn^{4+} ions are on octahedral sites. It must be borne in mind however, that the distribution found will be strongly stabilized by anion polarization. Magnetic measurements on these compounds are being carried out at present.

A discussion of the crystal chemistry of the materials reported in(1) and in the present communication will be given in a future paper.

Acknowledgement – The compounds $LiMe^{2+}_{0.5}Ti_{1.5}O_4$ were prepared by Mr. D. J. SCHIPPER, to whom our thanks are due.

G. BLASSE

Philips Research Laboratories
N. V. Philips' Gloeilampenfabrieken
Eindhoven-Netherlands

(2) A. DURIF and J. JOUBERT, *C. R. Acad. Sci. Paris* **255**, 2471 (1962).

(3) G. BLASSE, *J. Inorg. Nucl. Chem.* In press.

J Inorg Nucl Chem , 1963, Vol 25, pp 745 to 747 Pergamon Press Ltd Printed in Northern Ireland

BOOK REVIEWS

A I VOGEL **A Text-book of Quantative Inorganic Analysis** (including Elementary Instrumental Analysis) 3rd Ed Longmans, Green, London, 1962 Pp xxx + 1216 70s

VOGEL's "Quantitative Inorganic Analysis", especially since the appearance of the enlarged Second Edition in 1951, has become increasingly the standard English text-book on this subject for technical college students, undergraduates and post-graduate workers The new Third Edition appears in the same format as the Second and to the eye does not look much bigger, but it contains a wealth of additional material This has been made possible in part by the careful revision of the older text and in part by the addition of about 300 pages A close comparison of this edition with the previous one makes it immediately obvious that much re-writing has been carried out and the texts of even the most familiar determinations carefully revised, with resulting improvements in clarity

During the last decade, many advances have been made in the methods of quantitative inorganic analysis, both instrumental and in the use of new techniques and reagents It is fitting therefore that this new edition of "Vogel" should contain new chapters on Complexometric Titrations, Coulometric Titrations, Ion Exchange and Chromatographic Methods in Analysis, Emission Spectrographic Analysis, Flame Photometric Analysis, Solvent Extraction Methods of Analysis and High Frequency Titrations The new matter however is not confined to the new chapters, but one finds that new methods and techniques have been introduced into almost every chapter In short, this is both a major revision and an extension of the previous edition

In order to deal with the subject within a single volume, the Author has been compelled to exclude certain other important but lesser used techniques, such as X-ray methods, mass spectrometry, Raman spectrography, gas chromatography, radiochemical methods, nuclear magnetic resonance spectroscopy, polarimetry and refractometry These are best dealt with in specialist texts and this book is none the worse for their exclusion

The Author has aimed at providing a text-book which will be of value to the student throughout the whole of his training and in his subsequent career, to practicising analytical chemists and to all others who have occasion to utilise the methods of quantitative inorganic analysis This was an ambitious objective, but one which has been achieved This book is not only a reference book for a professional analyst, but can be recommended to anyone with an interest in the quantitative techniques of Inorganic Chemistry which should include anyone engaged in research in Inorganic Chemistry

F FAIRBROTHER

F A Ostroumov **The application of organic bases in analytical chemistry** (Translated from the Russian by D A Paterson) Pergamon Press London 1962

THE AUTHOR is from the Institute of Oceanology of the Academy of Science of the U S S R and this book is a collection of his investigations since 1935 From this research methods have been developed for the analysis of rocks, ores, mineral and marine deposits, and these methods have been tested in the laboratory of the All-Union Scientific Research Institute for Mineral Raw Materials as well as in the Institute of Oceanology

Much of this book is devoted to the use of the bases pyridine α-picoline and hexamethylenetetramine, and roughly one half of it deals with the precipitation of metals using pyridine alone or in the presence of its salts When hydrolysis is carried out with pryidine alone a pH of approximately 6 5 is established in the solution, and under these conditions Fe, Al, Cr, Ti, Zr, U, Th, In and Ga are precipitated in compact forms with low adsorptive properties Separation of these elements from

Mn, Ni, Co, Zn, Cu, Cd, Mg, alkaline earths and alkali metals can be effected by this means, since for the elements from Mn to Cd stable soluble complexes are formed with pyridine. By using pyridine in the presence of its salts a better control of pH is obtained, and, in the range pH 4.1 to 4.2, the separation of Bi from Pb, Cu and Cd can be achieved, whilst Th can be separated from Ce^{+3} and rare earth metals.

Some improvement is also claimed for the precipitation of Group IIIB sulphides when carried out from pyridine rather than from ammoniacal solutions. For example, nickel and cobalt sulphides are precipitated from pyridine solutions in crystalline forms which have low adsorptive properties and are not oxidized by air during filtration. Also the coprecipitation of alkaline earth carbonates with the sulphide precipitate is eliminated under these conditions since pyridine differs from ammonia and does not form carbonates. This method of separation is suggested for the removal of macro amounts of these elements from solution in the analysis of nickel and cobalt salts for copper, magnesium and alkali metals. By using pyridine-pyridinium chloride solutions it is possible to separate nickel and cobalt from manganese with hydrogen sulphide, since the pH of the solution is too low under these conditions to permit the precipitation of manganese sulphide. If the precipitation of manganese sulphide is required, this can be achieved from a solution of the sample containing hexamethylenetetramine. However, if this separation follows that of nickel or cobalt as sulphides, it is necessary to remove pyridine from solution before precipitating the magnanese. This procedure is recommended for the separation of manganese in the analysis of pyrolusite and other manganese rich materials for copper and magnesium, and in the analysis of manganese salts for alkali metals.

This book is of interest to Analytical Chemists who use the Classical Methods of Separation in applied analysis, especially for Group III elements. Sufficient practical details are included to enable anyone to carry out the separations, and in fact there appears to be some repetition of experimental details in some parts of the book. The translator has produced a readable text, and only minor misprints were observed. The book is well produced, but it is rather expensive.

G. W. C. MILNER

Advances in inorganic chemistry and radiochemistry. Vol 4, 1962

ONE of the problems facing authors of articles in series such as this is whether to set their subject in its historical perspective or to deal only with more recent work. Volume 4 of "Advances in Inorganic Chemistry and Radiochemistry" provides examples of both approaches. E. THILO, writing on "Condensed Phosphates and Arsenates", concentrates on a classical development of the understanding of these interesting compounds. This article would have been improved had a fuller account been given of recent physico-chemical and theoretical studies.

The opposite approach was taken by J. D. MACKENZIE who, in his account of "Oxide Melts", correlates the structures of these high temperature systems with their physical properties, and by J. R. MILLER reviewing "Recent Advances in the Stereochemistry of Nickel, Palladium, and Platinum". The latter gives a good account of this field and especially of the progress in the theoretical aspects of the problem. Unfortunately, the most exact theoretical treatment for nickel(II) in cubic symmetry (LIEHR and BALLHAUSEN, 1959) was not mentioned. Moreover, it would have been less confusing had the choice of x and y axes "between ligands" been stated earlier in the text, as the resulting strong field orbital diagrams are unconventional.

The potential overlap between this article and that on "Olefin, Acetylene, and π-Allylic Complexes of Transition Metals" by R. G. GUY and B. L. SHAW is, in fact, fairly small. The great interest shown in π-bonding ligands in recent years is effectively mirrored in this account, in which the main developments are set out element by element in systematic fashion. Nuclear magnetic resonance, which has proved to be a very powerful tool for studying such π-complexes, is itself reviewed in "The Use of Nuclear Magnetic Resonance in Inorganic Chemistry" by E. L. MUETTERTIES and W. D. PHILLIPS. This is an excellent discussion of the types of chemical information obtainable, and of the factors to be considered to avoid interpretational error. However, no mention was made of the method for determining the magnetic susceptibilities of very small volumes of solutions by nmr

The article on "The Chemistry of Polonium" by K W Bagnall provides a very readable account of the inorganic chemistry of this element The description of the techniques for handling intense α-emitters is especially interesting The volume is not free from printing, and other, errors, but these are of minor importance

D M L Goodgame

C K Jørgensen **Orbitals in Atoms and Molecules** pp viii + 162 Academic Press, New York, 1962 35s

This is a most unusual book First, the author has gathered together ideas from many different aspects of chemistry and has tried to form them into a unified whole, and, second, he has written in a highly characteristic style

Orbitals first—an orbital is a one-electron function, which is useful (though not necessary) in dealing with isolated atoms, with complexes showing small amounts of covalent bonding, with normal chemical bonds, and with solids Dr Jørgensen has described the nature of these orbitals and their increasing complexity as we proceed from simple atoms to regular solids His molecular studies are all within the molecular-orbital approximation which he asserts to be vastly superior to the valence-bond or electron-pair method The range covered in the twelve chapters of this book is immense No one working through these pages could fail to experience some feeling for the use of orbitals The analysis seems to the reviewer to be accurate, with the exception of some doubtful remarks concerning the use of the virial theorem for individual orbitals As might be expected of a person who had contributed so greatly to our knowledge of the theory of ionic complexes, this part of the book is more convincing than the rest

And now to the style for a textbook this is indeed most individual At times it seems as if the author wants to give us as complete a set of numerical values as is possible (some of his collected values will be most useful), and then suddenly we are told of some little personal incident and seem to be listening to the comments of someone who speaks aloud of his ruminations in the field of quantum chemistry Since the author has read so very widely, and obviously h is enjoyed thinking about modern concepts and models, these comments are often very stimulating, even if, as at times, they do not carry complete conviction There is relatively little normal "theory ' in this book, and it is not therefore suitable for a beginner But for those who do already posses a good deal of experience of the theories of molecular structure, and are themselves prepared mentally to "answer back" when they disagree with the author, this slim volume of 160 pages will provide a most valuable stimulus We need books like this one—but not too many of them!

C A Coulson

J Inorg Nucl Chem, 1963, Vol 25, p 748 Pergamon Press Ltd Printed in Northern Ireland

ERRATUM

TAICHI SATO The extraction of uranium (VI) from sulphuric acid solutions by di-(2-ethylhexyl)-phosphoric acid, *J Inorg Nucl Chem* **24,** 699-706 (1962)

Page 700, equation 1,

for "$UO_2^{2+}(a) + 2(HX)_2(o) \rightleftharpoons UO_2H_2X_4(o) + 2H^+(a)$"
read "$UO_2^{2+}(a) + 2(HX)_2(o) \rightleftharpoons UO_2X_4H_2(o) + 2H^+(a)$"

Page 705, sentence 2

for "The heat of reaction (i e the value of the enthalpy change) (1)"
read "The heat of reaction (i e the value of the enthalpy change) in equation (1)"

Page 706, acknowledgements, line 2

for "di-(3-ethylhexyl)-phosphoric acid" read "di-(2-ethylhexyl)-phosphoric acid"

J Inorg Nucl Chem 1963, Vol 25 pp 749 to 757 Pergamon Press Ltd Printed in Northern Ireland

HALF-LIFE OF ^{85}Kr*

J Lerner
Argonne National Laboratory, Argonne, Illinois

(*Received* 23 *October* 1962, *in revised form* 16 *January* 1963)

Abstract—The half-life of ^{85}Kr has been measured by observing the decay of the 0 7 MeV β-activity over a period of ten years, yielding the value 10 76 years This is somewhat higher than all of the values previously recorded in the literature Accuracy of the method and possible sources of systematic error are discussed

The half-life of ^{85}Kr has been measured by the direct decay method Samples of the active gas, mixed with inert krypton, were sealed in glass ampoules containing a thin window The 0 7 MeV β-activity escaping through this window was measured periodically with a proportional counter over a period of ten years An automatic counter was used to alternate sample and uranium standard measurements The mean value obtained was 10 76 ± 0 02 years (95 per cent confidence)

Aside from the intrinsic interest in the value of its half-life, ^{85}Kr has become of some importance both industrially(1 2) and scientifically Applications include its use as an inert gaseous tracer (i e , leak testing,(3) ventilation studies,(4 5) geochemical prospecting,(6 7) medical diagnosis,(8) etc), and as a convenient source of radiation (i e , polymerization of organic compounds,(9 10) static elimination,(11) light source,(12 13) thickness gauge,(14) etc) The half-life of ^{85}Kr enters into the calculation of fission-product yields,(15 16) and can be used to estimate nuclear reactor fuel burn-up (17)

The ^{85}Kr used in this measurement was extracted from the fission products produced by irradiation of natural uranium slugs in the Hanford reactor These slugs were exposed for about four months, then allowed to cool approximately one year Solution of the slugs took place in the presence of inactive krypton The krypton fraction was then removed and carefully purified from fission products and also from the other noble gases

---

* Based on work performed under the auspices of the U S Atomic Energy Commission

(1) F J Wilson, *et al* , AERE-I/R-2216,

(2) *Radiation A Tool for Industry*, Little, Cambridge, Mass AI I-52

(3) B Cassen and D Burnham, *Int Jour Appl Rad and Isot* , **9**, No 12, 54 (1960)

(4) C O Reiser and K L Wilson, *J Metals* **12**, 234–5 (1960)

(5) A H Howland, D E Kimber and R F Littlejohn *J Inst Heat Vent Eng* **28**, No 6, 57 (1960)

(6) W H Fleming and H G Thode, *Phys Rev* **92**, 378 (1953)

(7) S Amiel and L Winsberg, *J Nucl Energy* **5**, p 50 (1957)

(8) R J Sanders and A G Morrow, *A New Diagnostic Method in the Study of Congenital Heart Disease*, A/CONF 15/P/866, National Heart Inst , Bethesda, Md

(9) H S Miller and J H Zufall, *Fission Product Applications Using Gaseous Beta Sources*, NYO–2606 Air Reduction Sales Co , Murray Hill, N J

(10) W G Brown, Report TID-11574

(11) E Palmeri, Jr , H P Copeland and J G MacHutchin, *Development of Krypton 85 Static Elimination Equipment*, AECU–4363 United States Radium Corp Bloomsburg Penn

(12) P J Nowacki *et al* , *Polska Akad Nauk Inst Badan Jadrowych* 175/111, (1960) (Translated by J J Cornish, NP–tr–649)

(13) R Nampon, *Rev Gen Mécan* **43**, No 118, p 59 (1959)

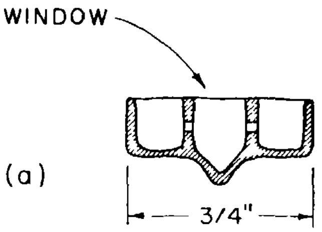
(14) W E Swift, *Nucleonics* **15**, No 3, 66 (1957)

(15) S Katcoff, *Nucleonics* **16**, No 4, 78 (1958)

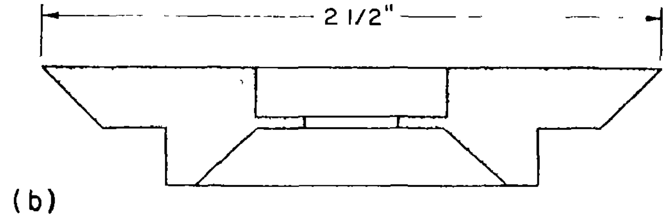
(16) S Katcoff, *Nucleonics* **18**, No 11, 201 (1960)

(17) ANL Chem Engng Div Summary Report, July, Aug Sept , 1960 (ANL 6231) p 42

The container for the ^{85}Kr samples consisted of a Pyrex "button" with a thin window (Fig 1a) Since the internal pressure was of the order of 10 cm it was necessary to support the window with an internal glass tube to resist atmospheric pressure The



CROSS SECTION OF
PYREX SAMPLE "BUTTON"



CROSS SECTION OF
BRASS SAMPLE HOLDER

FIG 1 —Krypton sample "button" and sample holder

glass buttons were cemented into a brass sample holder (Fig 1b), permitting the measurements to be made by an automatic sample-changing counter It was found necessary to coat the windows of the krypton sample buttons with a thin layer of conductive silver paint in order to prevent the build-up of static charges inside the proportional counter that would affect the counting efficiency

The standards consisted of chunks of natural uranium metal approximately 1 cm square by 1 mm thick These were cemented to 2 in aluminium disks for ease of handling, and were covered with several layers of silver paint This served to lower the counting rate to a level appropriate for the counter and also served to protect the uranium standards from possible mechanical or corrosion damage

The samples were counted in an automatic counter consisting of sample changer mechanism, proportional counter, amplifier, scaler with variable scaling ratio, high-voltage supply and printing recorder The sample changing mechanism contains a large wheel with tapered holes near the periphery for holding the samples (Fig 2a) A piston located beneath the edge of the sample wheel serves to raise the samples up into the counting chamber or to lower them back to the wheel The sample wheel is rotated by means of a Geneva mechanism engaging radial slots in the rim of the wheel

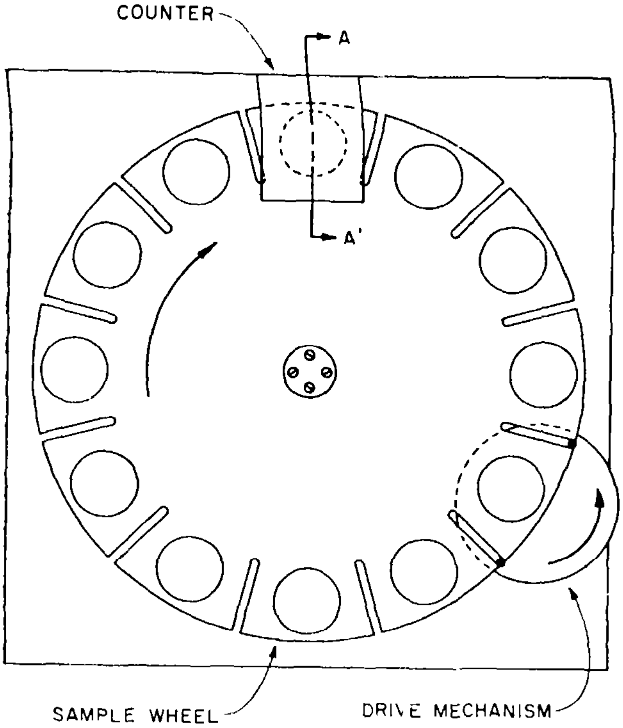


FIG 2a Plan view of sample changing mechanism

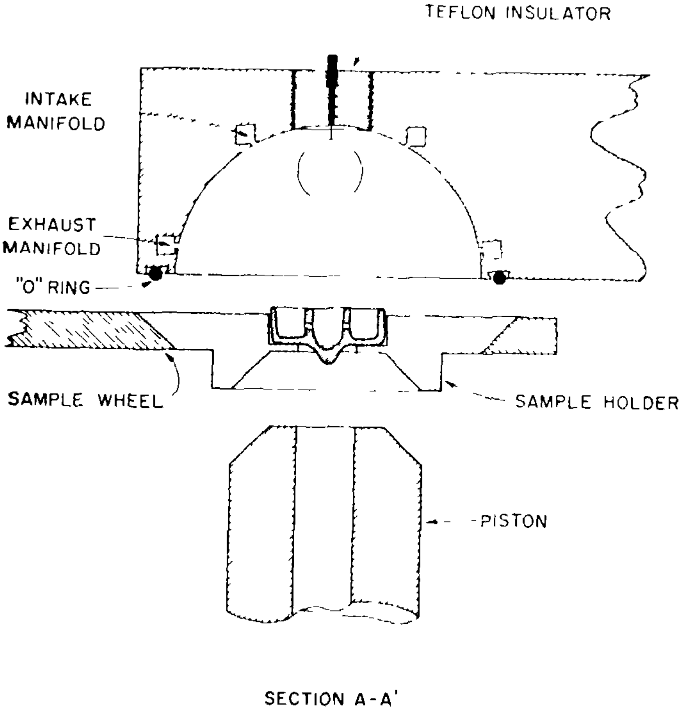


FIG 2b —Cross-section of counting chamber and sample changer

The proportional counter chamber is a hemisphere in which the sample mounting holder forms the bottom plate (Fig 2b) The assembly is rendered gas tight by means of an "o" ring Positive high voltage is brought in through a Teflon insert and terminates in a 2 cm diameter loop of 0 001 in stainless steel wire A manifold permits the counting gas to enter in the vicinity of the wire loop and another manifold located near the sample plate exhausts the gas through a bubbler to the atmosphere

The electronic circuitry associated with the counter is of standard construction, consistent with the present state of the art A special effort was made to promote the stability of the apparatus through the use of feedback amplifiers, stabilized high-voltage supplies, line voltage regulation, etc For most of the measurements the counter was operated inside of a shielded cubicle consisting of double walls of copper screening This served to isolate the equipment from false counts due to external electrical disturbances

At the beginning of a counting period the samples and standards are loaded onto the sample changing wheel, with the samples and standards alternating so as to effect an even distribution of intervals between standard counts For each of the twelve positions on the wheel there is a three-way switch that permits one of three options counting of the sample at a preset scaling factor, counting of the sample with no scaling (for background counts), or skipping of that position entirely The time interval for counting can be preset to any integral number of minutes between one and 440 However, the same counting time must be used for all of the samples and standards

In a typical measurement there are six samples and three standards, each counted for 100 min A background count is also taken for 100 min Since the counter functions on a 24 hr basis entirely without manual intervention, it is a simple matter to allow the machine to run long enough to accumulate sufficient counts on each sample to reduce the statistical error in the mean to a very low figure A typical value for the total counting time on each sample is 1000 min

The high-voltage versus counting rate plateaus for some of the krypton samples and the uranium standards are shown in Fig 3 For the krypton samples the average slope is of the order of $\frac{1}{3}$ per cent per 100 V, whereas for the uranium standards the slope is about $1\frac{1}{2}$ per cent per 100 V This variation in slope is to be expected, since the standards are relatively thick sources The considerable slope in the plateau characteristic of the standards is very desirable, however, since it means that the counting rate of the standards is very sensitive to changes in overall gain, whereas the krypton samples are relatively insensitive The plateau slopes can thus be used to correct the decay data for variations in counter efficiency

The corrected counting rates for the various samples, as a function of time, are given in Table 1 The counting rates were corrected for background, scaler resolution loss and gain variations The quoted error is the standard deviation as determined by variations from the mean at each point The time of the count is taken as the midpoint of the counting period It can readily be shown that for a short fraction of a half-life the middle of the counting period is substantially equal to the point in time where the average counting rate over the interval is the same as the true counting rate The zero point for the time scale was arbitrarily chosen as January 1, 1951

For each sample, the logarithm (base 10) of the corrected counting rates as a function of time was fitted to a straight line by the least squares process (Fig 4) The

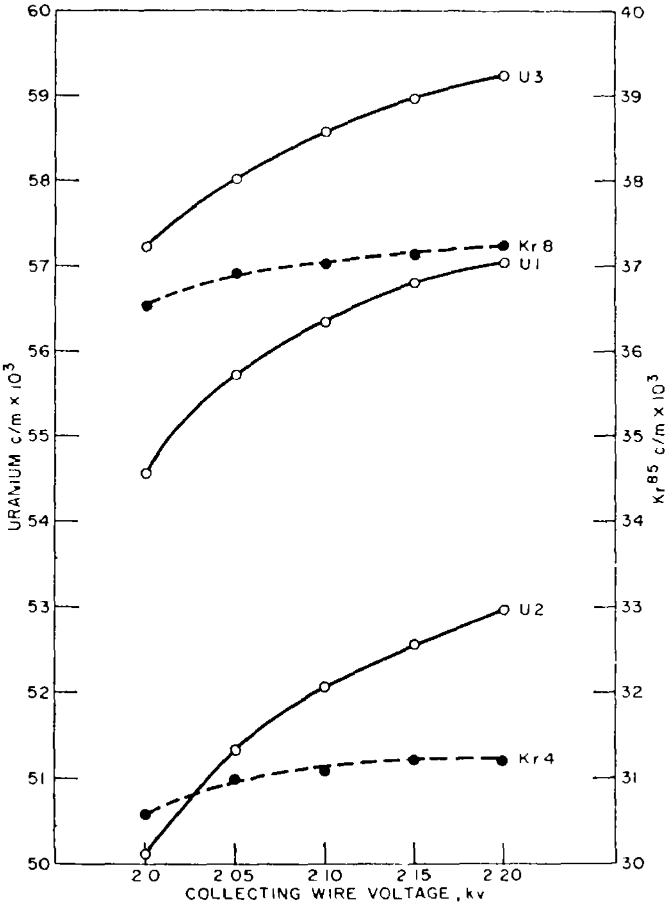


FIG 3 – Counting-rate plateaus for krypton samples and uranium standards

values obtained for the slopes and the external error of this slope are given in Table 2 The unweighted average is 10 76 ± 0 01 years (standard error) Although the magnitude of the calculated variances in the half-lives for each sample is roughly correlated to the slope of the sample plateaus, the application of Bartlett's test[18] does not contradict the assumption that the variances are indeed equal and that only chance fluctuations in the variances were observed Consequently, only the unweighted average is given

Other values previously reported in the literature are as follows The original measurement of HOAGLAND and SUGARMAN[19] gave 10 years with a quoted probable error of a factor of two In 1945 THODE measured the relative masses of ^{85}Kr to stable ^{84}Kr and ^{86}Kr with a mass spectrometer over an interval of six months and reported 9 4 ± 0 4 years[20] The mass ratio measurement was repeated in 1952 and the value

---

[18] A HALD, *Statistical Theory with Engineering Applications*, p 291 J Wiley, New York (1955) p 291

[19] E J HOAGLAND and N SUGARMAN, Radiochemical Studies The Fission Product (Edited by C D CORYELL and N SUGARMAN) Plutonium Project Record, Div IV, Vol 9, p 642 McGraw-Hill, New York (1951)

[20] H G THODE, *Nucleonics* 3, No 3, 23 (1948)

TABLE 1 KRYPTON SAMPLE COUNTING RATES RATES ARE COUNTS PER MINUTE QUOTED ERROR IS CALCULATED EXTERNAL STANDARD ERROR ZERO TIME IS JANUARY 1 1951

Date	Time (days)	Kr1	Kr4	Kr6	Kr7	Kr8	Kr10
9 7 51	250		56108 ± 13				
4 4 52	460	37232 ± 6	54053 ± 10				
4 10 52	466	37217 ± 6	54031 ± 13				
4 18 52	474	37190 ± 10	54010 ± 13				
6 21 52	538	36696 ± 13	53250 ± 16				
6 25 52	542	36754 ± 7	53350 ± 11				
8 30 52	608			14689 ± 6	17759 ± 7		
10 11 52	650	36039 ± 29	52240 ± 22	14511 ± 10	17561 ± 5		
10 17-52	656	35923 ± 8	52221 ± 20	14496 ± 5	17537 ± 4		
3 6 53	796	35112 ± 17	50978 ± 37	14170 ± 11	17139 ± 15	60614 ± 42	18916 ± 1
3-29 54	1184	32779 ± 21	47552 ± 30	13290 ± 9	16050 ± 6	56789 ± 22	17742 ± 1
10 1 60	3562	21596 ± 5	31310 ± 9	8721 ± 3	10535 ± 3	37426 ± 8	11780 ± 3
7 21 61	3855	20378 ± 7	29597 ± 9	8241 ± 5	9970 ± 5	35305 ± 11	10975 ± 7
8 5 61	3870	20328 ± 8	29562 ± 11	8228 ± 6	9947 ± 7	35282 ± 14	10968 ± 7

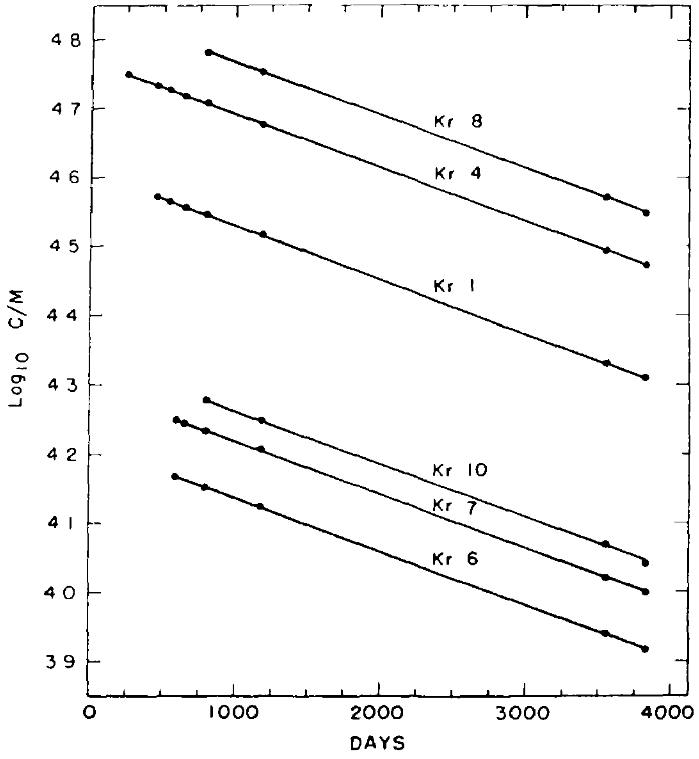


FIG. 4 —Decay curves for krypton-85 samples

10.27 ± 0.18 years was assigned (21) In this case, however, only one of seven measurements was made on the original gas sample, the other six measurements were mad on samples that were extracted from the uranium slugs at the time of the secon analysis. This introduces the possibility of error, in that if the irradiated slugs becam contaminated with atmospheric krypton over the seven year interval then the reporte value would be too low.

TABLE 2 — ^{85}Kr HALF-LIFE

Sample	Total decay time		Half-life	
	Days	Fraction of half-life	Corrected data (years)	Uncorrected data (years)
Kr1	3410	0.890	10.734 ± 0.008	10.716 ± 0.022
Kr4	3620	0.945	10.755 ± 0.016	10.724 ± 0.015
Kr6	3262	0.852	10.761 ± 0.027	10.740 ± 0.041
Kr7	3262	0.852	10.755 ± 0.028	10.734 ± 0.030
Kr8	3074	0.803	10.795 ± 0.029	10.763 ± 0.062
Kr10	3074	0.803	10.775 ± 0.087	10.742 ± 0.174
		Unweighted Average	10.763 ± 0.008	10.737 ± 0.007

Using the combination of a thin lens beta spectrometer and a scintillation detecto as a high-stability counter, TURNER measured the decay of ^{85}Kr over a six month perio in 1953 and reported(22) 10.57 ± 0.14 years. In 1954 BROSI and KETELLE(23) reporte 10.7 ± 0.2 years (95 per cent confidence), also using precision counting equipmen over a decay period of six months.

Since the value reported here is larger than all of the previously reported results the experiment and the data were carefully examined for possible inconsistencies o systematic error. In general, the corrections applied to the raw data were very small. The background count, for example, was usually quite close to 40 counts/min. Thi is entirely reasonable for the cosmic-ray background in a chamber of the size used i the counter. Since the background count was typically of the order of a few tenth per cent of the sample counting rate, it is unlikely that fluctuations or errors in th background count were of any importance.

The scalers used in the counting equipment had a resolving time of about 6 μsec corresponding to a value of the order of 10^{-7} min for τ in the correction formula

$$N_t = N_0(1 + \tau N_0),$$

where N_t is the true counting rate and N_0 is the observed counting rate. The resolutio correction for even the most active samples amounted to less than one-half of one pe cent of the sample counting rate. The resolution time was measured throughout th ten year interval and the values agreed to within 5 per cent, which is consistent with the expected statistical error in the τ measurement itself Once again, it seems unlikely that fluctuations or errors in the resolution correction can be of any consequence

---

(21) R. K. WANLESS and H. G. THODE, *Canad. J. Phys.* 31, 517 (1953).
(22) J. F. TURNER, AERE-N/R 1254 (1953).
(23) R. BROSI and B. H. KETELLE, ORNL 1674 p. 36 (1954).

The corrections for variation in counter gain were made by using the counting rates for the uranium standards to correct to a fiducial gain value As mentioned before, the corrections to the samples were relatively small, since the gas samples gave much better plateaus than the uranium standards In general, the corrections were only a few tenths per cent of the total counting rate

As an additional check on the validity of the gain corrections, the least-squares half-life calculation was performed on data uncorrected for gain variations The values obtained, together with the calculated external errors are also given in Table 2 The average value is 10 74 ± 0 01 years (standard error) Although the uncorrected data gives substantially the same value for $T_{\frac{1}{2}}$ as the corrected data, it should be noted that for the uncorrected data the variations of the points about the least squares lines, as measured by the calculated variances, are generally greater than the corresponding variations for the corrected data This in itself does not justify making the gain corrections, but does tend to confirm the validity of the corrections

An estimate of the stability of the counter can be obtained by examining the fluctuations in count for the same sample over a period of time The statistical error in the 100 min sample count was typically about 0 3 per cent For the krypton samples the ratio of calculated external error to the Poisson error averaged 2 2, while for the uranium standards the corresponding ratio averaged 3 6 Thus it is certain that the variations in counter efficiency exceeded the fluctuations due to normal statistical variations As expected, the uranium samples were more erratic than the krypton samples

The possibility of error in the time measurement should not be excluded Except for a possible arithmetic mistake, it is most unlikely there is an error in the time assigned to each point, since this is essentially a matter of recording the calender date There remains the possibility however, that the counting intervals were not constant, and that there was therefore an error in the counting rates The counter timing mechanism consists of a synchronous motor operating a gear train and a cam The cam closes an electrical switch once every minute A preset register counts the number of timing pulses and terminates the counting period when the correct number of pulses have been received The system was tested periodically by feeding pulses derived from the line frequency into the scaler, the recorded count indicated the timing was correct to within 0 01 min

For most of the measurements the power for the timing motor was derived from the laboratory timing line The frequency of this power is controlled by a tuning-fork oscillator to an absolute accuracy of the order of 50 p p m Even if the timing motor is operated from the normal power line, it has been our experience that the maximum drift in power line frequency over a period of 1000 min is also of the order of 50 p p m

The possible sources of systematic error have been carefully considered Presumably, the characteristics of the samples could have changed over the years so that the counting geometry was not constant Most of the plausible effects that one can think of, however, should tend to make the measured value for the half-life shorter rather than longer For example, sample leakage, sample adsorption on the walls of the container, release of occluded gas into the button, oxidation of the silver paint binder, sulphurization of the silver, etc , would all reduce the counting rate with time and would give apparently shorter half-lives

Contamination of the samples by some other activity seems most unlikely, primarily because the sample is a noble gas The activity would have to be an inert gas with a boiling point near that of krypton in order to survive the purification process The possibility that significant amounts of ^{81}Kr (2 × 10^5 years) were present was eliminated by a mass-spectroscopic analysis In addition, the presence of an activity with a different half-life would tend to produce curvature in the decay curve No such curvature was detected

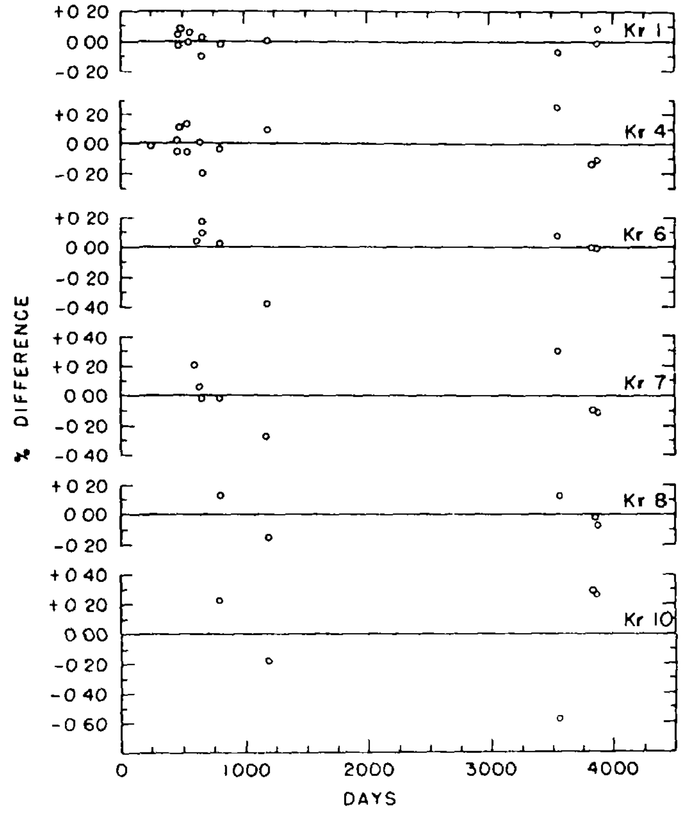


FIG. 5 Fluctuation of measured values about least squares lines

From the positive point of view, there are many reasons for accepting the half-life at its face value The method is basically a very simple one requiring only the use of a single instrument and considerable patience The corrections to the data are all very small, so that even a relatively large error in the correction would produce only a small error in the half-life Statistically, the fluctuations of the points about the least-squares lines were consistent with the fluctuations of the measurements at each point, and the fluctuations of the slopes about the mean value were consistent with the variations of the points about the least-squares lines Furthermore the points fluctuated at random about the lines, giving no evidence of "bunching" above or below the lines in any region (Fig 5)

J Inorg Nucl Chem , 1963, Vol 25, pp 759 to 762 Pergamon Press Ltd Printed in Northern Ireland

DISTRIBUTION OF RADIOACTIVE ANTIMONY FORMED BY NEUTRON CAPTURE IN ANTIMONY COMPOUNDS

J F Facetti*
Nuclear Science and Technology Division Puerto Rico Nuclear Centre†
Mayaguez, Puerto Rico

(*Received* 28 *October* 1962, *in revised form* 30 *December* 1962)

Abstract—Antimony compounds were irradiated with neutrons and the distribution of radioactive Sb^{122} and Sb^{124} between the tri and pentavalent oxidation states determined, after dissolving the samples in either fused potassium hydroxide or concentrated hydrochloric acid The results suggest that the new species reach their final oxidation state in the crystal, either during, or a short time after, irradiation In addition, the results show a linear relation between the composition of the oxide and the percentage of radioactive Sb(v) similar to that obtained by other workers with arsenic oxides

THE results of several other workers(1–4) on the distribution of the radioactive arsenic, formed by the (n, γ) processes on arsenic oxides, indicate the importance of carrying out similar studies with antimony oxides

Antimony, having similar properties to arsenic, forms three oxides commonly written as Sb_2O_3, Sb_2O_4 and Sb_2O_5 The irradiation of antimony gives the radioisotopes ^{122}Sb and ^{124}Sb, of known characteristics (5)

EXPERIMENTAL

A *Materials*

The irradiated antimony compounds were the three oxides and potassium antimoniate

The oxides used were Sb_2O_3 and Sb_2O_5 of ' pro-analysis ' grade, and Sb_2O_4 of spectroscopic purity They were used without further purification, the Sb_2O_4 was supplied by Johnson and Matthey (London, England)

In order to check the crystallographic identity of the oxides their X-ray diffraction patterns were measured by the powder method, using a conventional X-ray machine and identified by the ASTM data (6)

It was established that the irradiated Sb_2O_3 corresponds to the senarmontite structure (6,7) The Sb_2O_4 commonly known as antimony tetroxide is considered to be $SbSbO_4$,(7) and its X-ray patterns agreed with the reported data (8) The two irradiated pentoxides (Fisher Scientific and K and K Laboratories) did not have the same structure, as was indicated by their diffraction diagrams

---

* On leave of absence from the University of Asunción, Paraguay

† Operated by the University of Puerto Rico for the Atomic Energy Commission

(1) A G Maddock and M M de Maine *Canad J Chem* **34**, 441 (1956)

(2) H Kawahara and G Harbottle *J Inorg Nucl Chem* **9**, 240 (1959)

(3) G B Baro and A H Aten Proc Symp on *Chemical Effects of Nuclear Transformation* I A E A STI-PUB 34, Vol 2, 233 (1961)

(4) G B Baro, Thesis, Universidad de Buenos Aires (1961)

(5) D Strominger, J Hollander and G Seaborg Table of Isotopes Rev Mod Phys **30**, 585 (1958)

(6) X-Ray Powder Data File and Index to the X-ray Powder Data File

(7) Y K Syrkin and M Dyatkina, *The Structure of Molecules and the Chemical Bond*, pp 331-332 Butterworths London (1950)

(8) I Dihlstrom and A Westgren *Z Anorg Chem* **235**, 153 (1937)

The amounts irradiated were about 150 mg. It is difficult to obtain the oxides perfectly free of moisture. The oxides were accordingly oven dried at 120°C for several hours, and stored at room temperature *in vacuo*, in the presence of silica gel. The samples were sealed *in vacuo* in quartz or Pyrex ampoules and then irradiated.

Another compound irradiated was the commercial analytical grade "potassium pyro-antimoniate". The formula $KSb(OH)_6$ has been assigned to this compound.(9, 10) The samples were first submitted to the following treatments:

(A) One pair was heated at 285° for 20 hr, washed with ether and then heated to 285° for 48 hr. These samples were again heated to 500° for 20 min *in vacuo* in the ampoules before sealing off;

(B) Another pair were heated at 285° for 24 hr and then sealed in their ampoules;

(C) a third pair were heated at 130° for 24 hr before irradiation.

B. *Irradiations*

The samples were irradiated for 4 min at 36° in the PRNC nuclear reactor, with a neutron flux of 10^{12} cm^{-2} sec^{-1}.

C. *Chemical procedures*

Immediately or 24 hr after irradiation, the samples were dissolved in fused KOH in the presence of an appropriate inactive carrier, the solution was made 6F in HCl, and the Sb(V) extracted by shaking with isopropyl ether, in the presence of $MgCl_2$.(11) The samples were in contact with fused KOH for ½–1 min and then immediately cooled in ice.

Since Sb_2O_4 contains both forms of Sb(III) and Sb(V), no carriers were added for the separation. The Sb_2O_3 and $KSb(OH)_6$ were also dissolved in concentrated HCl at 60°C.

D. *Measurements and radiochemical purity*

The samples in acid magnesium chloride solution and in the ether solution were placed in calibrated polyethylene or Pyrex tubes and measured in a NaI (Tl) well crystal coupled to a multichannel analyser.

After the short lived isomers had decayed, the long lived isomers $T_{\frac{1}{2}}$ 2.8 days and $T_{\frac{1}{2}}$ 60 days of ^{122}Sb and ^{124}Sb were measured. In the analyses the gamma peaks of 0.57 and 0.69 MeV for ^{122}Sb, and of 0.60 and 1.69 MeV for ^{124}Sb were measured. The radiochemical purity was confirmed by following the decay. Since there is overlapping of the photopeaks at 0.57 and 0.60 MeV, these were resolved by following their decay rates and then substracting the extrapolated 60 day activity of the longer isomer.

RESULTS AND DISCUSSION

Table 1 shows the distribution of the radioactive ^{122}Sb and ^{124}Sb as Sb(III) and Sb(V).

The yield of Sb(V) in both samples of irradiated antimony pentoxide was the same and showed no apparent effect of their different structures. The distribution of ^{122}Sb and ^{124}Sb in the pentavalent state is essentially the same for all the compounds studied, within the experimental error. No isotopic effect is found in the chemical state of the two radioactive species, in agreement with the published data.(1, 12)

No difference exists between samples processed immediately or 24 hr after irradiation. Therefore, the isomeric transition ^{124m}Sb $T_{\frac{1}{2}}$ 21 min presumably does not bring about an increase in the yield of the higher oxidation state.

The results for Sb_2O_3 showed nearly 99 per cent retention, in agreement with previously published data.(1, 12) Retention in Sb_2O_5 was low and the yield of the pentavalent state in Sb_2O_4 was that expected for an equimolar mixture of Sb_2O_3 and Sb_2O_5,

---

(9) L. PAULING *J. Amer. Chem. Soc.* **55**, 1895 (1933).

(10) N. V. SIDGWICK *The Chemical Elements and their Compounds*, Vol. 1, P. 788. Oxford (1950).

(11) N. BONNER *J. Amer. Chem. Soc.* **71**, 3909 (1949).

(12) T. ANDERSEN and A. KNUTSEN *J. Inorg. Nucl. Chem.* **23**, 191 (1961).

TABLE 1

Compound	Solvent	Yield Sb(III)%		Yield Sb(V)%		Number of experiments
		Sb^{122}	Sb^{124}	Sb^{122}	Sb^{124}	
Sb_2O_3	KOH (Molten)	98.4 ± 0.4	98.3 ± 0.5	1.6	1.7	2
	HCl (at 60 °C)	98.2 ± 0.3	98.3 ± 0.4	1.8	1.7	2
Sb_2O_4	KOH (molten)	87.9 ± 1.1	87.5 ± 1	12.1	12.5	4
Sb_2O_5						
Sample I (K and K Lab.)	KOH (molten)	75.9 ± 0.8	75.9 ± 0.7	24.1	24.1	4
Sample II (Fisher Lab.)	KOH (molten)	76.5	76.8	23.5	23.2	1
$KSb(OH)_6$ treatment (a)	KOH	66.3	66.1	33.7	33.9	1
	HCl (at 60 °C)	67.2	67	32.8	33	1
treatment (b)	HCl (at 60 °C)	48.1 ± 2.6	48.1 ± 2.6	51.9	51.9	2
treatment (c)	HCl (at 60 °C)	29.1	29.5	70.9	70.5	1

The fusion with KOH (at 360 °C) apparently did not change the distribution between the two valence states as may be seen from the results of dissolving Sb_2O_3 in concentrated HCl. It follows that the majority of the radioactive Sb atoms reach their final oxidation state in the crystal lattice immediately after the nuclear process or possibly a short time after the practicle has lost its kinetic energy.[4] In terms of annealing, the fact that there is no change in the retention may be due to the short time at the high temperature in the melt. In addition, reaction between the sample and solvent must also be considered, since this can impede the recombination of recoil atoms with the "crystal vacancies". The neutralization is a rapid reaction. In addition the high concentration of OH in the fused KOH, will accelerate lattice degradation, via the intermediate formation of polyanionic complexes.[13] It must also be remembered that the vacancies occur as dilute impurities in the irradiated compounds.

The results for pretreated samples of $KSb(OH)_6$ suggest that the presence of the OH group in the irradiated molecule leads to a greater yield of the higher oxidation state. The low yield in case (A) can be attributed to the loss of water from the compound. The results in case (C) are in agreement with those recently published.[12]

It has been suggested that a linear relation exists between the yield of pentavalent radioactive arsenic and the ratio of oxygen atoms to arsenic atoms in the compound irradiated with neutrons.[3,4] A similar relation seems to hold for the radioactive pentavalent antimony formed in the irradiation of simple antimony compounds (See Fig. 1). This linearity, as in the similar case of radioactive arsenic, indicates that

---

J. L. AUDRIETH and T. MOELLER, *J. Chem. Educ.* 20, 219 (1943).

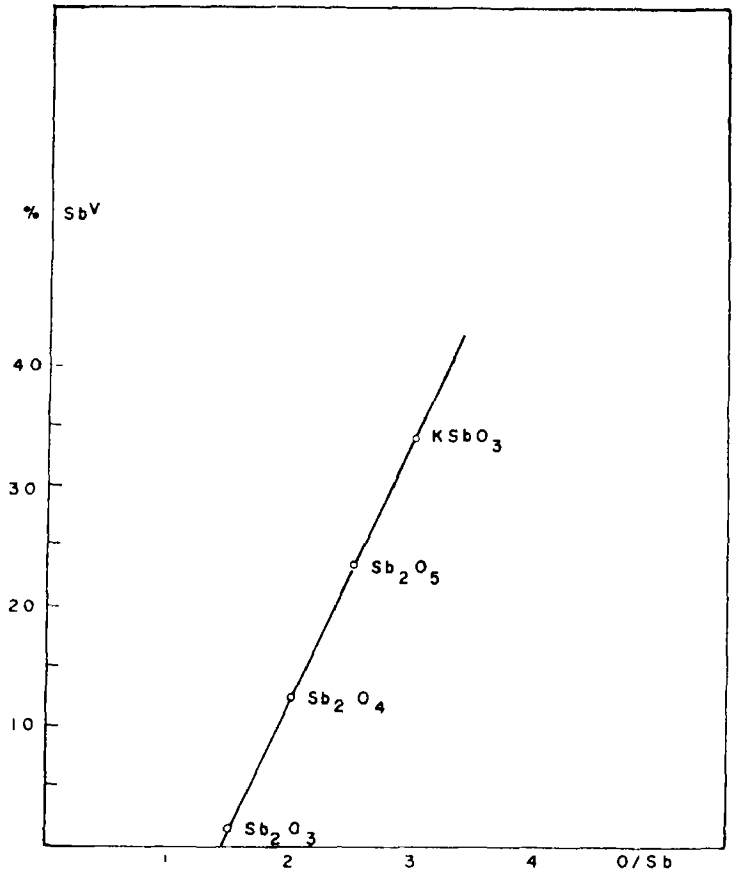


FIG. 1 —Yield of Sb(V)(%) vs oxygen to Sb ratio

the oxygen content of the compound is the main factor in determining the distribution of the radioactive antimony between the tri and pentavalent states A significant fact was that the results for $KSb(OH)_6$ submitted to pretreatment (A) fall on the linear relation at a point corresponding to the hypothetical $KSbO_3$

Acknowledgement—It is a pleasure to thank Dr G BARO of the Atomic Energy Commission of Argentina for helpful suggestions and F TRABAI and S TORRES of the PRNC for their collaboration in the chemical separations and measurements The author is also indebted to Dr F VAZQUEZ MARTINEZ who kindly performed the X-ray measurements and Dr O H WHEELER of the PRNC for several discussions

J. Inorg. Nucl. Chem. 1963. Vol. 25, pp. 763 to 770. Pergamon Press Ltd. Printed in Northern Ireland

ON THE AVERRED EFFECTS OF RADIOISOTOPIC TRACERS ON SOLUBILITY

R. W. RAMETTE and O. ANDERSON
Department of Chemistry, Carleton College, Northfield, Minnesota

(*Received* 22 *October* 1962)

Abstract—Contrary to recent reports (e.g., see reference (1)) on the effects of radioactivity on various heterogeneous chemical processes, barium sulphate labelled with ^{35}S having specific activities of 5, 20 and 50 mc/g showed constant solubility of 1.15×10^{-5} mole/l in water at 25°C. Calcium sulphate labelled with ^{45}Ca having specific activities of 0.1, 0.2, 0.5 and 1.0 mc/g showed constant solubility of 0.0151 mole/l. However, silver iodate, labelled with ^{110}Ag, behaved as though the radioactivity induces breakup of the crystal surface into particles too small for ordinary filtration, and the effect seems to depend on specific activity in the range 0.04–6.0 mc/g.

IN a series of articles which should unnerve all who use radioisotopes in heterogeneous chemical processes, V. I. SPITSYN† and his co-workers have declared(2) that various systems involving isotopic exchange, catalysis, adsorption, rates of solution and sublimation, corrosion and solubility are subject to striking changes in behaviour when radioactive materials are incorporated at normal tracer levels. Ostensibly the effects are due to the residue of positive charge on the solid surface after the emission of β-particles, and in some cases to the ionizing effect of such radiation on neighbouring atoms.

---

† Director, Institute of Physical Chemistry, Academy of Sciences, USSR.

(1) *Chem. Abstr.* **56**, 10967*f* (1962).

(2) These papers are available in English translation, but the following references show the original Russian pagination. With the one noted exception, all references are to the Doklady Akademii Nauk SSSR. Titles and bracketed comments are for the aid of readers interested in specific types of systems.

(a) V. I. SPITSYN and I. MIKHAILENKO, **121**, 319 (1958). Influence of the Intensity of the Radiation from ^{35}S on the Rate of Isotopic Exchange of Sulphur in the System K_2SO_4–SO_3.
(b) A. BALANDIN, V. SPITSYN, N. DOBROSEL'SKAIA and I. MIKHAILENKO, **121**, 495 (1958). Radioactive Catalysts. The Dehydration of Cyclohexanol on Magnesium and Sodium Sulphates. [Uses ^{35}S.]
(c) V. SPITSYN and V. GROMOV, **123**, 722 (1958). Effect of the Radioactivity of Barium Sulphate on its Sorptional Properties. [Uses ^{35}S; compares adsorption of acidic and basic dyestuffs.]
(d) I. MIKHAILENKO and V. SPITSYN, **131**, No. 1, 129 (1960). New Data on the Effects of Radioactive Solids on Heterogeneous Isotopic Exchange. [Higher specific activities of K_2 SO_4 compared to ref. a.]
(e) V. SPITSYN, E. TORCHENKOVA and I. GLAZKOVA, **132**, No. 3, 643 (1960). Effects of Radiation on the Solubility of Radioactive Solids. [Kinetics of solution and solubilities of $Ba^{35}SO_4$ of varying specific activity.]
(f) V. SPITSYN and N. MOSHANSKAYA, **133**, No. 4, 859 (1960). Effect of Specific Radioactivity of Cerium Oxalate on Its Solubility. [Uses ^{144}Ce.]
(g) V. SPITSYN, E. TORCHENKOVA and I. GLAZKOVA, **133**, No. 5, 1111 (1960). Solution of Barium Sulphate Labeled with Two Radioactive Tracers. [Kinetics of solution and solubilities using [illegible]Ba and/or ^{35}S.]

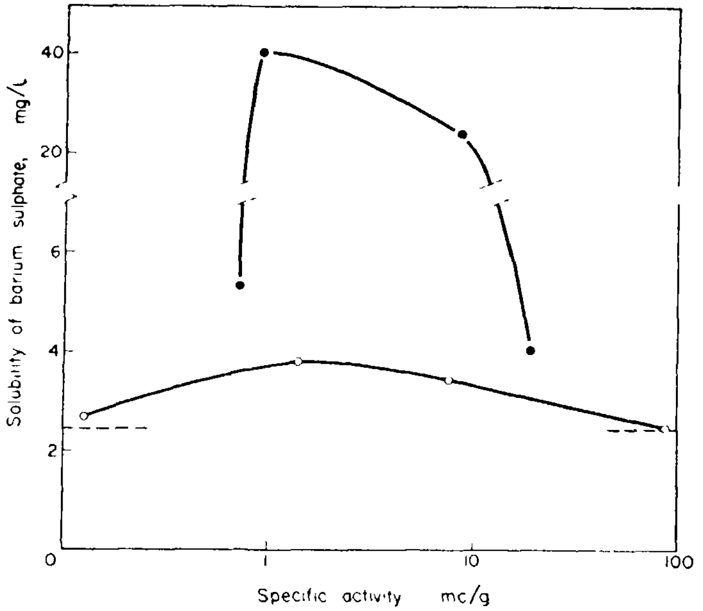


FIG 1 —Spitsyn's results on the effect of specific activity on the solubility of $BaSO_4$, labelled with sulphur-35 Top curve, sodium sulphate used in preparation of precipitate Bottom curve, sulfuric acid used Dashed line, solubility of non-radioactive barium sulphate

These conclusions are in startling contradiction to the basic premises of the tracer technique, namely, that isotopic species have identical chemistry except for the small effect of mass, and that the emitted radiation causes no detectable change in the system And the effects described in these papers are not small Fig 1 shows the reported effect of ^{35}S activity on the solubility of barium sulphate(2, 3g), with results as high as seventeen times the known solubility of non-radioactive barium sulphate, and with a

---

[h] A BALANDIN, V SPITSYN, N DOBROSEL'SKAYA and I MIKHAILENKO, **137,** No 3, 628 (1961) Radioactive Catalysts Dehydration of Cyclohexanol on Magnesium Sulphate and Calcium Chloride [Uses mixtures of $^{45}CaCl_2$ and $Mg^{35}SO_4$ to study reaction yield as a function of radiation energy at constant specific activity]

[i] V SPITSYN and I ZIMAKOV, **138,** No 1, 130 (1961) Effect of Radioactive Radiation from ^{90}Y and ^{91}Y on the Solubility of Yttrium Hydroxide

[j] L BELYAKOVA, V GROMOV, A KISELEV and V SPITSYN, **138,** No 5, 1139 (1961) Adsorption of Hexane and Benzene Vapours on Inactive and Radioactive Barium Sulphate

[k] V SPITSYN and I ZIMAKOV, **139,** No 3, 654 (1961) Effect of Radioactivity of Molybdenum Trioxide on the Velocity of Its Evaporation [Uses ^{99}Mo]

[l] I ZIMAKOV and V SPITSYN, **141,** No 6, 1400 (1961) Effect of Radiation Energy on the Sublimation Rate of Solids [Extends to work of ref k by incorporating ^{90}Y, ^{99}Mo and ^{185}W into MoO_3]

[m] V SPITSYN, *Izvestiya Akademii Nauk SSSR*, Otdelenie Khimicheskikh Nauk, No 8, 1325 (1960) New Data on the Effect of Radioactive Radiation on Solids and External Radiation on Some Heterogeneous Chemical Processes [See reference 1] Somewhat of a review article, with extensions of several studies reported in the foregoing references]

[n] V SPITSYN, K YANDUSHKIN, S BALEZIN and I KULESHOV, **143,** 1406 (1962) Investigation of Atmospheric Corrosion of Radioactive Samples of Armco Iron and Steel 2 [Uses ^{59}Fe]

severe superposed effect of the method of precipitation. The latter immediately suggests that the precipitates were differently contaminated through coprecipitation. A second example is shown in Fig. 2, where the reported solubility of cerium (III) oxalate depends linearly upon the logarithm of the ^{144}Ce specific activity (2f). In this case we would criticize the arbitrary extrapolation to log s.a. equal to −6 to obtain a solubility value at "infinitely low activity(2m)" for the purpose of comparison with known solubility values for the non-radioactive salt. As a final example dealing with

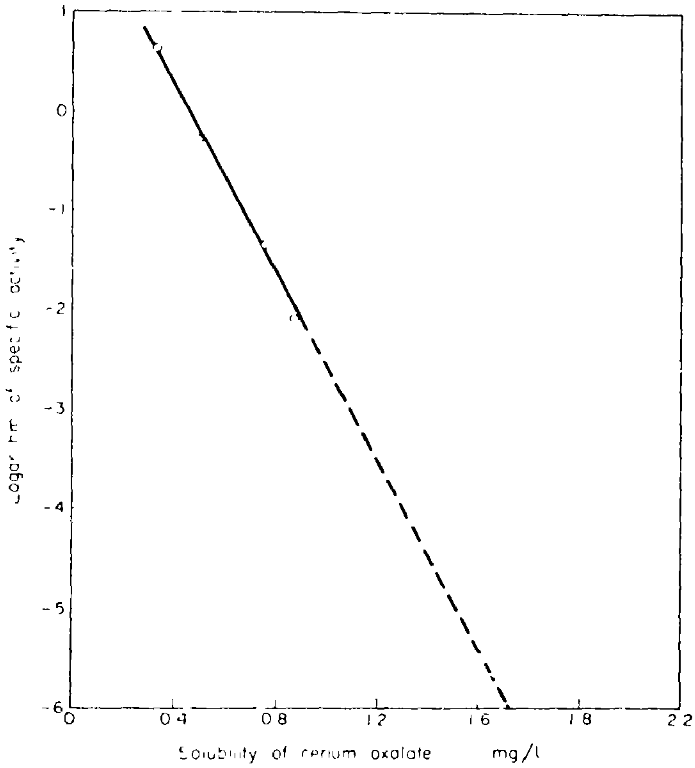


Fig. 2.—Spitsyn's results on the effect of specific activity on the solubility of cerium-144 oxalate.

solubility, Fig. 3 reproduces the findings for the solubility of yttrium oxide as a function of the ^{90}Y and ^{91}Y specific activity (2i). The concluding statement in this paper is as follows: "Following are some preliminary considerations regarding the mechanism of the phenomena observed in this work. As a result of the emission of β-particles positive point charges are formed on the surface of the Y_2O_3 solid phase. These affect the negatively charged OH groups of the incompletely ionized $Y(OH)_3$ molecules in solution. This is the reason for the decrease in the solubility of yttrium hydroxide in the presence of the radioactive isotopes ^{90}Y and ^{91}Y. When the emission of β-particles reaches a certain high level, ionization effects increase under the influence of bombardment by electrons, and this apparently includes dissociation of the $Y(OH)_3$ molecules. Repulsion of Y^{3+} ions from the positively charged surface of the solid Y_2O_3 should lead to an increase in the solubility of yttrium hydroxide preparations having a high specific radioactivity. Only when the specific radioactivity of the Y_2O_3 samples was very low (less than 0.1 mc/g) did the presence of the radioactive isotope have no effect on the solubility of the compound."

Although some of these results have been obtained with highly radioactive materials (e.g., up to 260 mc/g in the cerium oxalate case) most of the work has been with relatively low level labelling as commonly used in tracer applications. Therefore it is curious that such effects have failed to achieve recognition during the past countless

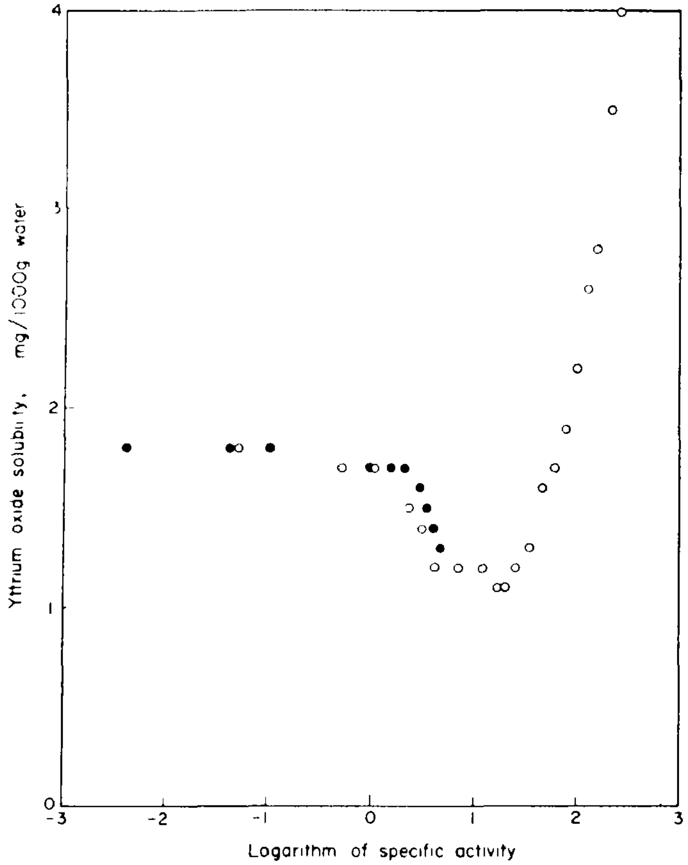


FIG. 3. Spitsyn's results for the solubility of yttrium oxide in water. Open points, using ^{90}Y as tracer. Closed points, using ^{91}Y.

applications of radioisotopes. Nevertheless, because these workers have reported impressive radioisotope effects in a wide variety of situations, and because it seems unreasonable to try to explain them all away as merely the "study of artifacts", and because the implications of these results are of tremendous importance to radioisotope technology, it seemed eminently worthwhile to initiate independent studies, which we have limited to solubility measurements on inorganic salts.

Because of work which had been in progress in this laboratory, the first study dealt with the solubility of silver iodate, labelled with ^{110}Ag, using γ-scintillation counting. The results so far indicate that there are indeed special problems associated with radioactive salt compared to non-radioactive silver iodate. This work has been unexpectedly troublesome from an experimental standpoint, is still incomplete, and wil be described only briefly in this paper. The main substance of this report is concerned with the solubility of calcium sulphate containing ^{45}Ca (0.26 MeV β, $t_{1/2}$ = 163 dys), and the solubility of barium sulphate containing ^{35}S (0.17 MeV β, $t_{1/2}$ = 87 dys).

EXPERIMENTAL

Calcium-45 was obtained from Oak Ridge as $CaCl_2$ in HCl solution. At the start of this study the specific activity was about 4 mc/g. A stock solution of non-radioactive calcium chloride was standardized via titration with primary standard EDTA solution and also gravimetrically as silver chloride. Calibrated volumetric ware was used in the preparation of solutions of labelled calcium chloride with specific activities of 0.1, 0.2, 0.5 and 1.0 (nominal values) millicuries per gramme of calcium. These solutions served as a source of standards for counting as well as in the preparation of calcium sulphate precipitates. At first the precipitation was carried out by adding a 5 per cent excess of sodium sulphate with vigorous stirring. The fine precipitate was allowed to age for a day, and was filtered and washed on fine sintered glass. Later it was decided to repeat the entire study with an improved product resulting from precipitation from homogeneous solution. For this, the calcium was first complexed with EDTA, which prevented precipitation when excess sulphate was added. Then an excess of nickel nitrate was added and the pH was immediately adjusted to four. With gentle heating the nickel slowly replaced the calcium in the chelate, and the precipitate consisted of large crystals which settled rapidly. No significant difference was found in the solubilities of the two types of precipitates, indicating that the ageing of the "ordinary" products had been successful in removing adsorbed impurities.

Approximately 0.2 g samples of the calcium sulphate precipitates were equilibrated with 30 ml portions of redistilled water in polyethylene capped borosilicate tubes by rotation in an air bath at 25°C. A time study indicated that the system with non-radioactive material came to equilibrium in a few minutes, but rotation was continued for several hours in each case.

Ten-ml portions were centrifuged for a few minutes, and because of the low temperature coefficient of solubility it was judged that no significant change in concentration would occur during this step. From the supernatant liquid microlitre samples were taken with calibrated pipettes, evaporated on planchets, and counted. Also, two-ml samples were taken for titration with 0.01 M EDTA, using calcon as indicator at pH 12.

Sulphur-35, carrier free, was obtained from Oak Ridge as sulphate in HCl solution. A stock solution of sodium sulphate was standardized gravimetrically as barium sulphate. Labelled sodium sulphate solutions were prepared having specific activities of 5, 20 and 50 mc/g of sulphur. These were used as sources for counting standards and also for precipitation of barium sulphate samples. Several varied attempts to precipitate barium sulphate from homogeneous solution failed to yield crystals particularly better than those obtained by very slow addition of 50 ml of 0.04 M barium chloride to 50 ml of 1 M perchloric acid containing 2 mmoles of sulphate, with magnetic stirring at 90°C followed by digestion.

Approximately 0.1 g samples were equilibrated with 30 ml of water as with the calcium sulphate. At first, sampling was accomplished with the aid of centrifuging, but later the samples were filtered through VC Millipore filters with no significant change in results. Because of the low solubility titration analysis was not possible, and 100-lambda samples were evaporated and counted. Because the results were about 15 per cent higher than expected, the samples were aged and digested further. The results given below are for barium sulphate which had been digested at 100°C for about 16 hr followed by rotation with water for about 30 hr.

For each sample in both studies, at least 10,000 counts were taken to insure reasonable statistical accuracy. A Nuclear-Chicago D-47 gas-flow detector (with micromil window) was used. Standards were repeatedly prepared and recounted, and count rates were always well within the linear region of Geiger detection.

RESULTS AND DISCUSSION

Table 1 summarizes the results obtained for the concentration of calcium ion, equal by inference to the molar solubility of calcium sulphate in the saturated solutions of the precipitates which were obtained from homogeneous solution.

TABLE 1. SOLUBILITY OF CALCIUM SULPHATE AT 25°C, USING VARIOUS SPECIFIC ACTIVITIES OF CALCIUM-45

^{45}Ca (mc/g Ca)	Solubility (mole/l.) By EDTA tit'n	Solubility (mole/l.) By counting ^{45}Ca
0	0.0152	--
0.1	0.0152	0.0150
0.2	0.0152	0.0150
0.5	0.0151	0.0150
1.0	0.0151	0.0150

Clearly there has been no effect of labelling on the solubility of this salt. The values are constant within experimental errors (since such small samples were taken for the EDTA titrations) and in good agreement with what we consider the best literature[3] value, 0.0153, for non-radioactive material.

However, it is noted that this is a relatively soluble compound, whereas the type of effect being tested might be expected to be more prominent with very slightly soluble compounds when small losses by adsorption of negative ions on the positive surface of the crystals would be more significant compared to the concentration in solution. But one worthy conclusion from the calcium sulphate results is that the techniques of radioisotope labelling and counting used in this work seem reliable.

The results for the barium sulphate study are listed in Table 2, and refer to the concentration of sulphate ion (assumed to be equal to solubility) obtained by ^{35}S counting.

TABLE 2. SOLUBILITY OF BARIUM SULPHATE AT 25°C, USING VARIOUS SPECIFIC ACTIVITIES OF SULPHUR-35

^{35}S (mc/g S)	molar solubility × 10^5
5	1.15
20	1.16
50	1.14

These values are not only constant, but are in fair agreement with the precise conductivity work of ROSSEINSKY,[4] who found $1.038 \pm 0.005 \times 10^{-5}$ M for the solubility of a product resulting from the very slow mixing of large volumes of boiling, very dilute solutions. In terms of milligrammes per litre, his result is 2.42, while ours is 2.68, a difference of 10 per cent. These figures may be compared with Fig. 1, which refers to work at 20°C. Thus, our results fail to confirm any noticeable effect of specific activity on barium sulphate solubility, a reasonable hypothesis being that SPITSYN's precipitates may have been contaminated with coprecipitated sodium sulphate as a result of mixing 0.1 N solutions of sodium sulphate and barium chloride.

The results of the silver iodate solubility study, using silver-110 in the specific activity range from 0.04 to 6.0 mc/g have been recorded by HOFFER.[5] This work is not ready for detailed publication, and is being continued. Briefly, the radioactive precipitates (prepared from homogenous solution as large crystals) have behaved differently from the non-radioactive salt. With the latter, equilibrium was reached in an hour or so, and the results of iodometric titration were consistent with the best literature value. However, in the first stage of the work the apparent solubilities of the radioactive samples quickly exceed the expected value, and upon continued rotation and sampling rose fairly steadily at the rate of about 1 per cent per day for 10 days. HOFFER had been sampling by allowing the dense crystals to settle for a few hours, vacuuming the floaters from the surface, and then pipetting without filtering. This failure to reach steady values indicated that perhaps the tumbling process was causing the crystals to abrade with the production of motes too small to settle in the time allowed. The time study was repeated with the addition of pressure filtration through fine sintered glass, including precautions against loss by adsorption. This did not make a great difference, and a newly-prepared precipitate of specific activity 0.037 mc/g exhibited the weird behaviour of showing a sharp concentration increase after about 2 hr, going through a maximum at about 20 hr of almost nine times the expected value, and dropping back down to more normal levels after 100 hr. We were certainly reminded of the strange kinetics of solution effects observed by SPITSYN(2e, 2g). Although we cannot claim to have reached equilibrium with these solutions, Fig. 4 shows the values of apparent solubility obtained after 6–12 days of rotation. The next phase of this work will employ Millipore filters to test the view that the radioactive samples are subject to break-up of

---

[3] G. A. HULETT and L. E. ALLEN, *J. Amer. Chem. Soc.* **24**, 674 (1902).

[4] D. R. ROSSEINSKY, *Trans. Faraday Soc.* **54**, 116 (1958).

[5] J. K. HOFFER, Senior Thesis, Carleton College (1962).

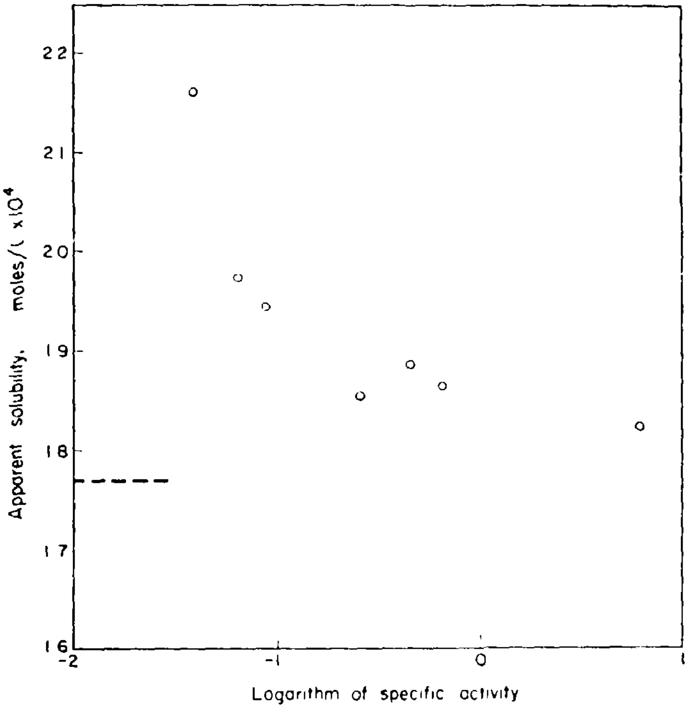


FIG. 4.—Hoffer's results on apparent silver iodate solubility, using ^{110}Ag. Dashed line, value expected from studies of non-radioactive silver iodate.

the crystal surface with the production of tiny particles too small for ordinary filtration. In this connection we should point out that SPITSYN has shown[6] by electron microscopy that the surface of radioactive potassium sulphate crystals is "loose, with projections and depressions resembling the corrosion picture".

In conclusion, we are reassured as to the applicability of radioactive tracers in solubility studies, but we will treat with newly-emphasized caution and respect the problems associated with the preparation of precipitates and the sampling of saturated solutions. We do not feel that the present work has settled the matter comfortably, and are reminded that solubility is only one of the heterogeneous processes reported to be subject to previously unsuspected radioisotope effects. It seems important that this matter should be studied fully.

Acknowledgement—This work was supported by a National Science Foundation grant for scientific research, and also by the NSF Undergraduate Research Programme.

(6) V. I. SPITSYN, *Soviet Chemistry Today* (p. 107). A series of six lectures published by the National Academy of Sciences—National Research Council, Washington, D.C. (1961).

J Inorg Nucl Chem 1963 Vol 25, pp 771 to 777 Pergamon Press Ltd Printed in Northern Ireland

THE PERBROMATE PROBLEM

D S URCH
Queen Mary College, London E 1

(*Received* 4 *October* 1962, *in revised form* 19 *January* 1963)

Abstract - The σ and π bonding in the anions XO_4^{n-} formed by non-metallic members of the second and third rows of the periodic table is examined in some detail Evidence is found for efficient π-bonding from Si, P, S and Cl Also in these elements the 3s-orbital is progressively more tightly bound so that the σ bonds are weakened Perchlorate especially depends on good π bonding for its existance The radial functions for 3*d* and 4*d* hydrogen-like atomic orbitals are considered and it is concluded that 4*d*-orbitals will be much less efficient at π bonding than 3*d*-orbitals Since the σ framework for perbromate will be similar to that for perchlorate the absence of good π bonding is fatal The chemistry of these and related anions is interpreted in the light of these theories

CHEMICAL bonds may be formed between atoms when the following conditions are fulfilled (1)

(1) orbitals belong to the same symmetry class,
(2) orbitals overlap efficiently,
(3) the energies of the orbitals are similar

Group theory will determine condition 1 (2–5) Outside the first row of the Periodic table it is not always easy to determine whether condition 2 can be fulfilled Whilst the angular portions of atomic wave functions are often described the radical function is commonly ignored Yet it is this function that will be vital in determining whether a given atomic orbital (A O) can or cannot overlap well with another A O In this paper the efficiency with which 3*d* and 4*d*-orbitals can overlap with nearby 2*p* oxygen orbitals will be considered in some detail The third condition may result in quite good overlap contributing only a negligible amount to the overall stability of the molecule As with radical A O functions it is not always easy to calculate the exact levels of atomic orbitals when they are making bonds However, estimates based on atomic spectra(6) give a rough idea of the energies of atomic orbitals (7)

π-bonding with second row elements

First row elements are characterized by planar anions such as CO_3^{2-} and NO_3^- whilst in the second row very stable tetrahedral anions SiO_4^{4-}, PO_4^{3-} SO_4^{2-} and ClO_4^- are formed The absence of tetrahedral oxy-compounds from the first row is not due to steric reasons for esters of ortho-carbonic acid, C(OR)$_4$, are known The stability of second row anions XO_4^{n-} may therefore be due to the presence of vacant 3*d*-orbitals on the central atom to which the excess negative charge on the oxygen atoms may be donated by means of π-bonding (8 12) Group theory shows that the *d*-orbitals (E and T_2) have the right symmetry properties for overlap with lone pair orbitals on the oxygen atoms (E, T_1 and T_2)(13) Bonding is therefore possible Oxygen is a strongly electron attracting element so the σ-bonds will be distorted towards the oxygen atoms, leaving the *d*-orbitals of the central atom more exposed to the nucleus than in the free atom The *d*-orbitals will therefore be more tightly bound and reduced in size In overlap with oxygen 2*p*-orbitals these effects will lead to more efficient bonding (conditions 3 and 2 respectively) (10) π-bonding would thus seem to offer an explanation of the exceptional stability of these second row tetrahedral oxy-anions Further evidence in support of this argument is the correlation between π-bond order and bond length found by CRUICKSHANK(14)

---

(1) C A COULSON, *Valance*, p 71 Oxford (1952)
(2) R S MULLIKEN, *Phys Rev* **43**, 279 (1933)
(3) J E ROSENTHAL and G M MURPHY *Rev Mod Phys* **8**, 317 (1936)
(4) H EYRING, J WALTER and G E KIMBALL, *Quantum Chemistry* p 172 & 227 J Wiley, New York (1944)
(5) M A MELVIN, *Rev Mod Phys* **28**, 18 (1956)
(6) C E MOORE, *Tables of Atomic Energy Levels* (National Bureau of Standards Circular No 467) U S Gov Printing Office Washington D C (1949–52)
(7) H H JAFFE, *J Chem Educ* **33**, 25 (1956)

σ-bonding

The above discussion of π-bonding presupposes that the tetrahedral anions are firmly held by an underlying σ-bond network based on "sp^3 hybrids" of the central atom orbitals VAN VLECK(15) has shown that if the difference in energies between the *s* and *p*-orbitals is large then the assumption of sp^3 hybridization gives erroneous molecular orbital energy levels, even though it does give an adequate description of the electron distribution about the atom When the complete secular determinant for the molecule is written down, terms such as $\int\psi_{x_1}H\psi_{x_2}$ (where, $\psi_{x_1} = \frac{1}{2}(\phi_{x_s} + \phi_{x_{p_x}} + \phi_{x_{p_y}} + \phi_{x_{p_z}})$, $\psi_{x_2} = \frac{1}{2}(\phi_{x_s} + \phi_{x_{p_x}} - \phi_{x_{p_y}} - \phi_{x_{p_z}})$, two sp^3 hybrids from x) are not equal to zero, as required by simple valence bond theory, but to one quarter of the energy difference between *s* and *p* A Os

In Fig 1 are plotted the relative energy levels of atomic orbitals for various atoms, determined by the method of JAFFÉ(7) from atomic spectra

Since the purpose of this paper is to consider the stability of various tetrahedral structures, the energies of the molecular orbitals (M Os) must be determined as accurately as possible It can be seen from Fig 1 that the *s*-*p* energy separation is very large for many atoms and the assumption of sp^3 hybridization would introduce large errors Also since *s* and *p*-orbitals correspond to irreducible representations of a regular tetrahedron the use of basic A Os is simpler than the use of hybrids

In XO_4^{n-} the 2*s*-orbitals of the oxygen are so tightly bound that they may be ignored Bonding will be due to the 2*p*-orbitals One such orbital from each oxygen may be supposed to be directed at X These four orbitals combine to form molecular orbitals of symmetry A_1 and T_2 On X the *s* orbital has symmetry A_1 and the three *p* orbitals T_2 Condition 1 is thus fulfilled for σ-bonding In the absence of

---

(8) L PAULING, *The Nature of the Chemical Bond* (2nd Ed) p 241 Cornell, Ithica, N Y (1944)

(9) L PAULING, *J Phys Chem* **56**, 361 (1952)

(10) W MOFFIT, *Proc Roy Soc* **200** A, 409 (1950)

(11) D P CRAIG, A MACCOLL, R S NYHOLM, L E ORGEL and L E SUTTON *J Chem Soc* 332 (1954)

(12) H H JAFFÉ, *J Phys Chem* **58**, 185 (1954)

(13) G E KIMBALL, *J Chem Phys* **8**, 188 (1940)

(14) D W J CRUICKSHANK, *J Chem Soc* 5486 (1961)

(15) J H VAN VLECK, *J Chem Phys* **1**, 177 (also 219) (1933)

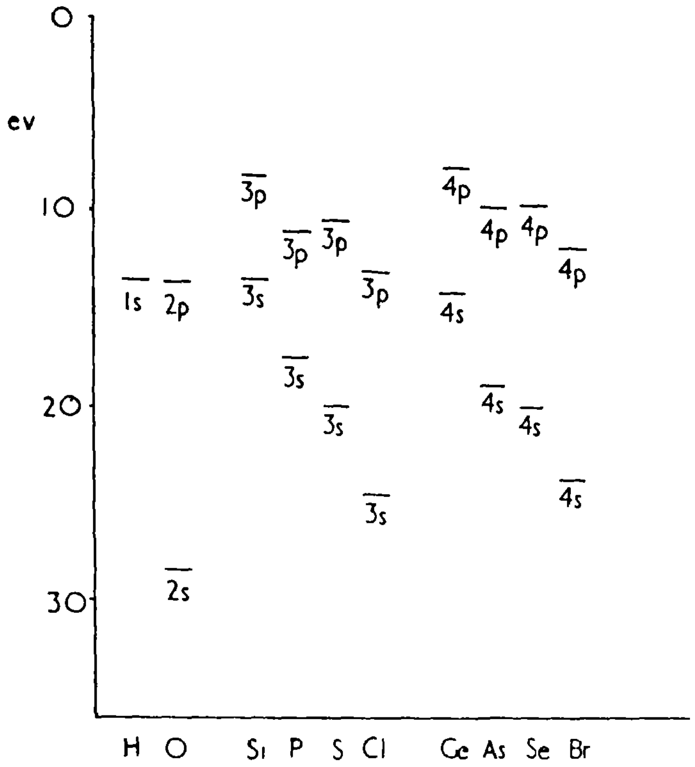


FIG. 1 —Valence shell orbital energy levels (eV)

evidence to the contrary it seems reasonable to suppose that condition 2 is also met but as can be seen from Fig. 1 the energy match for A_1 overlap progressively worsens from silicon to chlorine (also from germanium to bromine) Indeed for chlorine it is probable that the 3s orbital plays little or no part in the bonding of the oxygen atoms The assumption that the tetrahedral oxy-anions have a strong σ-bonded foundation becomes less and less true from silicate to perchlorate The stability of these anions depends increasingly on the efficiency of the π-bonding This is clearly seen both in the bond length contraction* (see tables, References 8, 14) and also in their general chemistry (16)

Where p-d π-bonding is very important for the stability of the molecule any reduction in that bonding should lead to a decrease in stability Thus with silicon reduction of p-d-bonding by the formation of second bonds to the oxygen atoms proceeds freely, leading to amphiboles, micas and silica itself For phosphorus, too, such polymerization is possible ($P_2O_7^{4}$, $(PO_3)_n^{n}$ etc) but is not so widespread, nor are the products so stable With sulphur a further reduction, both in readiness of polymerization and stability of polymer (e g $S_2O_7^{2}$ $(SO_3)_3$, $(SO_3)_n$ etc) is observed and with chlorine the formation of just one covalent bond turns an anion stable to 400°C (e g $KClO_4$) into a dangerously explosive compound (e g $HClO_4$, Cl_2O_7, etc)

---

* This contraction may also be due to the d-orbitals experiencing stronger nuclear field from Si to Cl so that more effective π bonding results[12,14]-condition 3

General references to Inorganic and Structural Chemistry are from N V SIDGWICK *Chemical Elements and their Compounds* Oxford (1950), and A F WELLS *Structural Inorganic Chemistry*, (3rd Ed) Oxford (1962)

3d and 4d atomic orbitals

Since the pattern of valency *s* and *p* A.O. energy levels is similar for analogous second and third row elements, it will be of interest to apply the ideas so far developed to the anions GeO_4^{4-}, AsO_4^{3-}, SeO_4^{2-}, BrO_4^-. The same reduction of σ-bond strength will occur and the stability will depend increasingly (from left to right) upon the efficiency of $4d$-$2p$ π-bonding. Condition 1 is fulfilled and the inductive effect of the four oxygens will ensure that 3 is also met. In order to determine whether condition 2 can also be fulfilled some estimate of the relative radial functions for $3d$ and $4d$-orbitals is necessary. The simplest approximation to the radial functions for atomic orbitals is due to SLATER.$^{(17)}$ These functions are most useful when considering bonding between orbitals subject to a reasonably large effective nuclear charge (Z). Under this condition the nodes of the atomic orbitals will be drawn very close to the nuclei and out of the bonding region. The nodes may therefore be safely ignored. Such is not the case for the $3d$ or $4d$-orbitals, considered in this paper, which are well screened from the nucleus (Z say 3). For these orbitals a more accurate description than the Slater approximation will be necessary.

In Fig. 2 normalized hydrogen-like radial functions (R_{nl}) are plotted for $3d$ and $4d$-orbitals for various values of Z.$^{(18)}$ It is reasonable to use hydrogen-like wave functions for this preliminary study, rather than the more accurate Hartree-Fock self-consistent field functions$^{(19)}$ since the two have a qualitative similarity and since bond formation will cause distortion of the atomic orbitals rendering the Hartree-Fock refinements for an isolated atom irrelevant.

In order to estimate the strength of the d-p π-bonding the integral $\int \psi_p H \psi_d \, d\tau$ should be calculated. However, it is often assumed that the resonance and overlap ($\int \psi_p \psi_d \, d\tau$) integrals are proportional$^{(20)}$ and the latter are usually easier to find. Since in the molecules under consideration the $2p$-orbital of oxygen and the angular functions of the d-orbitals are constant, a comparison of the $3d$ and $4d$ radial functions at the critical distance (1.5–2.5 Å) will permit a qualitative estimate of $\int \psi_{2p} \psi_{3d} \, d\tau$ and $\int \psi_{2p} \psi_{4d} \, d\tau$ to be made. The ratio of these two integrals will be a measure of the relative efficiency of $2p$-$3d$ and $2p$-$4d$ π bonding.

If it is supposed that the effective Z for $3d$-orbitals of a 2nd-row atom surrounded by four oxygen atoms is not greatly different from the effective Z for the $4d$-orbitals of the 3rd-row analogue in a similar situation, then a direct comparison of the radial functions, as shown in Fig. 2, can be made. From Fig. 2 it can be seen that $3d$-orbitals will be most efficient at π bonding when $Z \sim 3$. But for the same Z the node of the $4d$- orbital is so placed as to make $\int \psi_{2p} \psi_{4d} \, d\tau \simeq 0$. Thus it may be concluded that because of a difference in radial atomic wave functions the $4d$-orbitals will be much less efficient at π bonding with $2p$-orbitals than $3d$-orbitals in comparable situations.

---

(17) J. C. SLATER, *Phys. Rev.* **36**, 57 (1930).

(18) L. PAULING and E. B. WILSON, *Introduction to Quantum Mechanics*, p. 135. McGraw-Hill, New York (1935).

(19) S. R. HARTREE, *The Calculations of Atomic Structures*, J. Wiley, New York (1957).

(20) R. S. MULLIKEN, *J. Amer. Chem. Soc.* **72**, 4493 (1950); C. A. COULSON, *Valence*, p. 83. Oxford 1952; H. EYRING, J. WALTER and G. E. KIMBALL, *Quantum Chemistry*, p. 213. J. Wiley, New York (1944); L. PAULING, *The Nature of the Chemical Bond* (2nd Ed.) p. 76. Cornell Ithica, New York (1944).

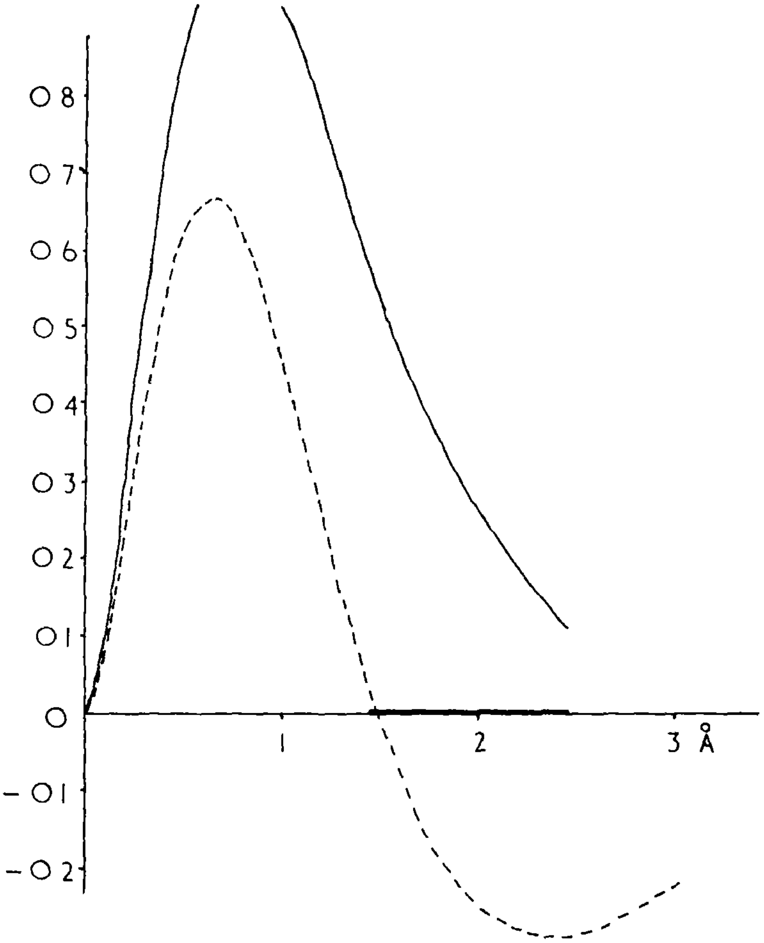


FIG. 2(a).—Normalized hydrogen-like radial functions for various values of effective nuclear charge (Z)

Key - (a) (Z/a_0) 8, $Z \sim 4$
(b) (Z/a_0) 6, $Z \sim 3$
(c) (Z/a_0) 4, $Z \sim 2$
—— 3*d* - - - -4*d*

The distance coordinate is shaded where the oxygen 2*p*-orbitals will be of maximum importance for π-bonding

The chemistry of 3rd row elements in XO_4^{n-}

If these conclusions are true those ions which depend on 4*d*-2*p* π-bonding to make up for deficiencies in σ-bonding will be unstable or unknown. The series germanate, arsenate, selenate, perbromate should be marked by increasing instability, as is in fact observed. In germanate and arsenate the lack of good π-bonding has little effect on stability (A_1 M.O. is still contributing to σ bonding) but a greater tendency to polymerization and colloid formation is observed for arsenate when compared with phosphate. Selenate is markedly less stable than sulphate, and is more easily reduced. Perbromate is not known. It is for the halogen tetra-oxy anions that the σ-skeleton is

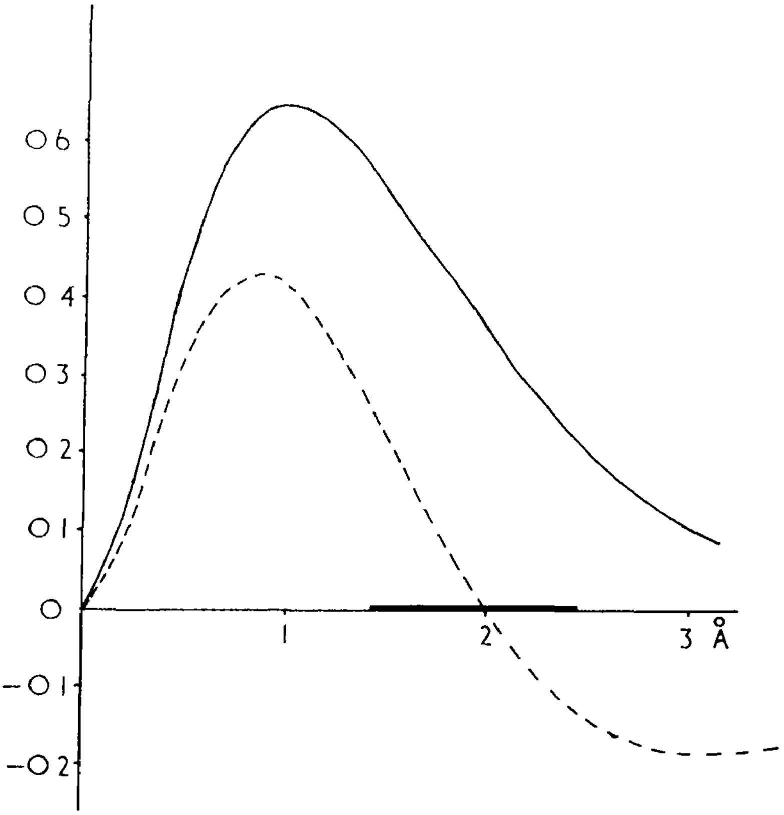


FIG 2(b)

weakest and most in need of π-stabilization But the $4d$-orbitals of bromine are inefficient at π-bonding and so perbromate is unstable A further effect of the weakness of $4d$-$2p$ π-bonding is the small difference between the Schomaker-Stevenson corrected bond lengths and the true bondlengths (Table 1)

Further discussion of the chemistry of 2nd and 3rd row oxy-compounds

Other oxy-anions besides XO_4^{n-} are known, e g sulphite, chlorate etc Since p-d π-bonding depends on electronegative elements being attached to the central atom

TABLE 1 – BOND-LENGTHS IN XO_4^n (Å)

XO_4^n	1 Covalent radii sum	2 (1) with SCHOMAKER-STEVENSON correction[21]	3 Observed bondlength
GeO_4^{4-} (as $(GeO_3)_n^{2n-}$)[22]	1.96	1.80	1.84
AsO_4^{3-}[23]	1.95	1.81	1.75 ± 0.5

---

[21] V SCHOMAKER and D P STEVENSON, *J Amer Chem Soc* **63**, 37 (1941)

[22] Y GINETTI, *Bull Soc Chim Belg* **63**, 460 (1954)

[23] L HELMHOLZ and R LEVINE, *J Amer Chem Soc* **64**, 354 (1942)

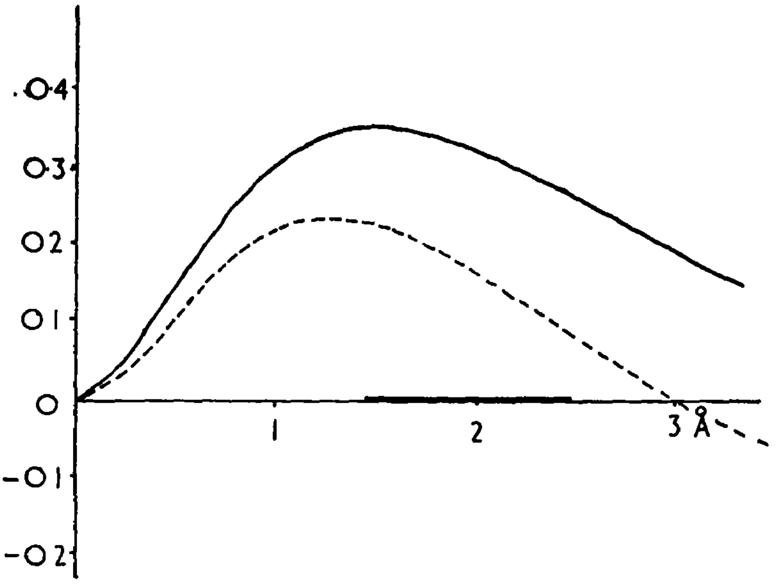


FIG 2(c)

the efficiency of this bonding will decrease in a series such as ClO_4^-, ClO_3^-, ClO_2^- ClO^- Chlorine-oxygen bond lengths for the first three are 1 46, 1 48, 1 57 Å, this extension might well be due to a relaxation of π-bonding

In the tetrahedral case the σ-bonds were weakened if the central atom A_1 A O became too tightly bound However, XO_3^{n-}-type anions have C_{3v} symmetry, the central atom valence A Os being, s, A_1 p_z, A_1 p_x & p_y, E The three p-orbitals pointing towards X from the surrounding oxygen atoms are in groups A_1 and E Three strong σ-bonds can therefore be formed from X's three p-orbitals and the lone pair will remain in the s, A_1-orbital Thus for XO_3^{n-}, XO_2^{n-}, XO^{n} p-d π-bonding will never be necessary, in the sense that it is necessary for perchlorate Also, ignoring for the moment π-bonding, the tendency to form XO_3^{n} instead of XO_4^{n-} will increase as the s orbital becomes more tightly bound

This is clearly shown in the chemistry of these elements Silicon does not form an ion of the type XO_3^{n-} With phosphorus a hydrogen is bonded to the "lone pair" so that PO_3^{3-} is unknown, the ion is the tetrahedral HPO_3^{2} (cf H_2PO_2) Sulphite is well known but is easily oxidized to sulphate and the "lone pair" can also pick up hydrogen to form tetrahedral HSO_3 in concentrated solution (24)

Chlorate is far more stable and is only oxidized to perchlorate with difficulty A very similar gradation of properties is found with the third row elements Germanites possibly based on GeO_3^{4-} are at best rare and unstable Arsenites are easily oxidized to arsenates By contrast selenites and bromates are much more stable The addition of π-bonding to this picture should make the 2nd row XO_3^{n-} anions more stable than their 3rd row analogues Thus, for example, the heat of formation (ΔH_f°) of $HClO_3$ (aq) is -24 kcal mole^{-1} but that of $HBrO_3$ (aq) is only -12 kcal mole^{-1} (25)

Indeed the existence of such ions as sulphite, chlorate, selenite and bromate with

---

R M GOLDING, *J Chem Soc* 3711 (1960)

Handbook of Chemistry and Physics, 40th Ed , 1864 and 1867, Chemical Rubber Publishing Co , Cleveland, Ohio, U S A (1959) lone pairs of electrons is good evidence that one pair of electrons is in fact tightly bound It can be seen from Fig 1 that the ease of oxidation of SO_3^{2-}, SeO_3^{2-}, ClO_3^-, BrO_3^-, is roughly related to the tightness with which the s A O is bound (even though the stability of the product is governed by other factors)

A similar effect is found even in the first row of the peridic table where the oxygen 2s-orbital is tightly bound and plays little part in covalent bond formation, oxygen has a maximum covalency of three but for nitrogen and carbon it is four

Since at least three covalent bonds may be formed with ease by all the elements considered in this paper ions such as XO_2^{n-}, XO^{n-} will be subject to ready oxidation

4th row elements, Sn, Sb, Te, I

The chemistry of these elements is often nearer to the second row member of their group than to the third row member, (e g PCl_5, $SbCl_5$, no $AsCl_5$, ClO_4^-, IO_4^- no BrO_4^-) yet it seems probable that the σ-structures of analogous compounds will be similar and that 5*d*-orbitals will be no more efficient than 4*d*-orbitals at π-bonding It might well be that 4*f* and not 5*d*-orbitals are used It is hoped to make this topic the subject of a later paper

J Inorg Nucl Chem, 1963, Vol 25 pp 779 to 781 Pergamon Press Ltd Printed in Northern Ireland

SINGLE CRYSTAL DATA OF SOME TETRAMERIC ALUMINIUM ALKOXIDES

E L AMMA
Department of Chemistry, University of Pittsburgh, Pittsburgh 13, Pa

(*Received* 1 *November* 1962)

Abstract—Single crystal data of aluminium alkoxides are reported The alkyl groups are methyl, ethyl, and isopropyl The unit cell of aluminium isopropoxide is consistent with a tetrameric entity but not with a chain type of polymer

THE aluminium alkoxides, $Al(OR)_3$, have been known for some time to exist as tetramers in benzene solution[1,2] This together with the small dipole moment in benzene suggests a closed structure similar to that proposed by SUTTON and SIDGWICK[3] for TlOR, Fig 1 Recently the Tl atom positions have been verified by single crystal X-ray diffraction[4]

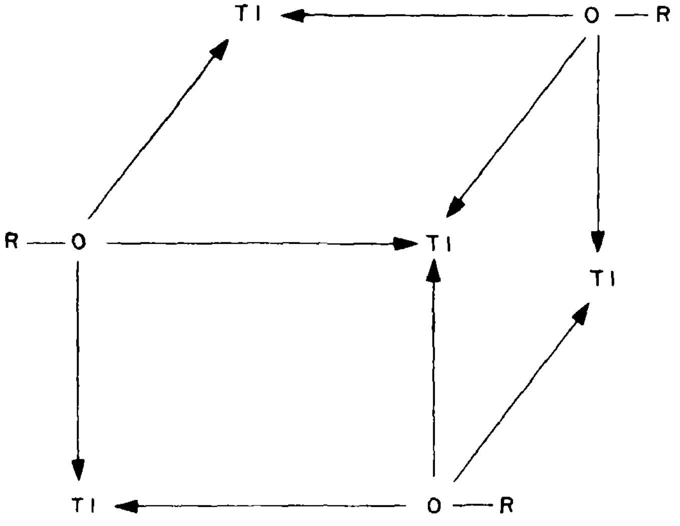


FIG 1

Of course, in the presence of the many electron Tl atoms the oxygen and carbon position could not be determined by X-ray diffraction Hence the oxygen atoms could be at the cube corners, co-ordinated to three Tl atoms in $TlOCH_3$ or to three Al atoms in $Al(OR)_3$, alternately the oxygen atoms could be situated along the face diagonal of the cube and bonded to two metal atoms Provided that the usual difficulties in a structure analysis can be overcome the oxygen and carbon positions should be determinable in the aluminium alkoxides

[1] R A ROBINSON and D A PEAK, *J Phys Chem* **39**, 1125 (1935)
[2] H ULICH and W NESPITAL, *Z Phys Chem* **165**, 294 (1933)
[3] N V SIDGWICK and L E SUTTON, *J Chem Soc* 1461 (1930)
[4] L F DAHL, Private communication (1962)

The fact that the melting points of many of the aluminium alkoxides are high ~100°C compared to the boron analogues, which are generally liquids, is consistent with some sort of polymer in the solid state. In the course of our investigations of metal alkoxides, we have obtained single crystals of some aluminium alkoxides suitable for diffraction studies.

EXPERIMENTAL

The crude aluminium alkoxides were prepared from the appropriate alcohol and aluminium amalgam by the procedure given by ADKINS.(5) The crude compounds were then treated in a variety of ways depending upon the alkoxide, in attempts to obtain single crystals.

$Al(OCH_3)_3$: insoluble, infusible powder: no single crystals could be grown.

$Al(OC_2H_5)_3$—crude compound was extracted in a soxlet extractor and solvent removed under vacuum. Under these conditions this compound readily forms glasses in ethanol, hexane, carbon tetrachloride and most common solvents. Vacuum sublimation was also unsuccessful. Perhaps partial crystallization of the glass is the cause of the ageing effect.(6) Single crystals were obtained by rapid cooling of the solution from the ethanol extraction, but they were never completely free of glassy material.

$Al(OiC_3H_7)_3$: crude material extracted with hexane in a soxlet extractor and solvent removed under vacuum. Readily forms good single crystals.

Crystals were sealed in thin walled glass capillaries for diffraction data. Densities were measured by flotation in hexane-carbon tetrachloride mixtures. Lattice parameters were determined by back-reflection techniques with CuKα radiation.

RESULTS

$Al(OC_2H_5)_3$ Monoclinic $a = 12.17 \pm 0.01$ Å $\beta = 93°$
$b = 28.70 \pm 0.01$ Å
$c = 19.98 \pm 0.03$ Å

Systematic extinctions
$h0l$, $h + l = 2n$ only present
$0k0$, $k = 2n$ only present

Space group $P2_1/n$
$Z = 24$ molecules/unit cell
ρ observed 0.95 g/cm³
ρ calc 0.93 g/cm³

$Al(OiC_3H_7)_3$—Tetragonal $a = b = 12.59 \pm 0.005$ Å
$c = 32.00 \pm 0.005$ Å

Systematic extinctions
$00l$, $l = 4n$ present only
$h00$, $h = 2n$ present only

Space Group $P4_12_12$
$Z = 16$ molecules/unit cell
ρ observed = 1.07 g/cm³
ρ calc 1.07 g/cm³

---

(5) H. ADKINS, *J. Amer. Chem. Soc.* **44**, 2178 (1922).

(6) D. C. BRADLEY, *Progress in Inorganic Chemistry*, Vol. 2 (Edited by F. A. COTTON) New York: Interscience (1960).

DISCUSSION

Aluminium isopropoxide is the most tractable problem in terms of a single-crystal structure analysis The 16 Al atoms can be placed in two sets of the eightfold general positions Placing the Al atoms in these positions places certain restrictions upon the nature of the polymer in the solid state An infinite polymer extending along the 4_1 axis is ruled out because of the large *c*-axis A similar argument in terms of distances rules out infinite polymers in the *a*, *b* plane and inclined to the *a*, *b* plane However, the existence of a tetramer is consistent with the space group $P4_12_12$

We have obtained complete three-dimensional Weissenberg data for the aluminium isopropoxide and are proceeding to solve the structure

Acknowledgement - This research supported by A E C contract AT (30 1) 2669

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 783 to 787. Pergamon Press Ltd. Printed in Northern Ireland

X-RAY STUDY AND THERMOELECTRIC PROPERTIES OF THE USi_xGe_{3-x} SYSTEM

L. H. BRIXNER
E. I. du Pont de Nemours & Co. Pigments Department
Wilmington, Delaware

(*Received* 12 *December* 1962)

Abstract—A series of solid solutions of USi_3 and UGe_3 has been prepared to demonstrate that complete solid solubility exists, with dependence on Vegard's Law. The electrical resistivity, Seebeck coefficient and thermal conductivity have been determined to characterize the compositions in the USi_xGe_{3-x} system by their thermoelectric Figure of Merit.

Most transition metal silicides are metallic conductors. Semiconducting transition metal silicides such as $CrSi_2$ and $ReSi_2$ are rather rare.[1] Since only 66·66 per cent of all atoms in a disilicide are silicon, whereas in a trisilicide we have 75·00 per cent silicon on an atomic basis, it was of interest to see if a trisicicide such as USi_3 would exhibit semiconducting properties.

Trisilicides are quite rare, and only two or three species are mentioned in the literature. Buddery and Welch[2] first indicated the existence of $IrSi_3$. Bahn and Schubert[3] reported hexagonal lattice parameters for this trisilicide. Brauer and Haag[4] first mentioned USi_3, which was later confirmed by Frost and Maskrey[5], who described the simple cubic structure of both USi_3 and UGe_3. The uranium has twelve nearest Si or Ge neighbours in this structure at a distance of $a_0/\sqrt{2}$, whereas the Si and Ge have four nearest U atoms at the same distance. The fact that the trigermanide and trisilicide of uranium are isostructural afforded the possibility for complete solid solubility in the system USi_xGe_{3-x}; therefore, we undertook to study the structural and thermoelectric parameters of the system in the hope that the thermal conductivity of the solid solutions might be reduced as had been demonstrated in the Si/Ge system.[6]

To complete the list of trisilicides, we should also mention $BaSi_3$. Wohler and Schuff[7] gave some evidence for the existence of this compound. In some of our own experiments, we prepared a barium silicide by arc-melting the constituents (Found, Ba) 62·5, Si, 36·8% (Ba : Si = 1 : 2·9). It is an n-type semiconductor yielding a complex X-ray pattern free from lines of the elements. The pattern indicated low symmetry and could not be interpreted structurally without work on single crystals.

---

[1] V. S. Nesphor and G. V. Samsonov, *Soviet Physics* **5**, 877–880 (1960).
[2] J. H. Buddery and A. J. E. Welch, *Nature, Lond.* **167**, 362 (1951).
[3] S. Bahn and K. Schubert, *Z. Metallkunde* **51**, 327 (1960).
[4] G. Brauer and H. Haag, *Z. Anorg. Chem.* **259**, 197–200 (1949).
[5] B. R. T. Frost and J. T. Maskrey, *J. Inst. Metals* **82**, 171–80 (1953–4).
[6] M. C. Steele and F. D. Rosi, *J. Appl. Phys.* **29**, 1517–1520 (1958).
[7] L. Wohler and W. Schuff, *Z. Anorg. Chem.* **209**, 33–59 (1932).

EXPERIMENTAL

The solid solutions described in this paper were prepared either by the powder-metallurgical technique of sealing the high-purity components (weighed to the nearest milligram) in quartz ampoules and heating to 1200°C for 20–30 hr, or by direct combination in an arc melt. Each technique has advantages and disadvantages. In the first case, the reaction product is a powder which can be pressed easily into any desired shape but the compact needs to be sintered subsequently to develop strength. Depending on the sintering temperature, the densities obtained by this treatment varied between 80 and 95 per cent of theoretical. Arc-melted buttons, on the other hand, were essentially 100 per cent dense but required machining in order to obtain any desired geometry. For compositions high in germanium concentration, the first route was generally preferred because of Ge losses during arc-melting. The compacted bars were sintered by inductive heating in a water-cooled copper boat.

Crystallographic characterization

Samples for X-ray studies were generally taken from the centre of molten specimens. They were crushed in an agate mortar to a particle size of −325 mesh. Powder diffraction patterns were taken with a Phillips 114.6 mm diameter camera at 25°C. The samples were sealed in 0.2 mm diameter Lindemann glass capillaries and were exposed to the K_α radiation of copper ($\lambda = 1.5418$ Å) for between 4 and 6 hr. Densities were determined by vacuum-distilling CCl_4 onto the sample contained in a 5 ml pycnometer. The parameters given in Table 1 can be considered accurate to ±0.005 Å. If the parameters or the densities given in the Table are plotted as a function of composition a straight line will be obtained, indicating a Vegard's Law dependence is observed. For USi_xGe_{3-x}, a_0 can be expressed as the following function of x:

$$a_0 = -0.0455x + 4.196 \pm 0.005$$

TABLE 1. LATTICE PARAMETERS OF THE USi_xGe_{3-x} SYSTEM

x	Comp.	a_0 (Å) X-ray	a_0 Å (calc.)	Unit cell volume (Å^3)	ρ (X-ray) (g ml^{-1})
0	UGe_3	4.196*	4.196	73.88	10.245
0.5	$USi_{0.5}Ge_{2.5}$	4.170	4.173	72.51	9.929
1	$USiGe_{2.0}$	4.153	4.151	71.63	9.535
1.5	$USi_{1.5}Ge_{1.5}$	4.128	4.128	70.34	9.184
2.0	$USi_{2.0}Ge$	4.104	4.105	69.12	8.812
2.5	$USi_{2.5}Ge_{0.5}$	4.081	4.082	67.97	8.417
3	USi_3	4.060*	4.059	66.92	7.997

* These parameters are in good agreement with those previously reported by FROST and MASKREY (l.c.).

Electrical properties and thermal conductivity

In order to evaluate these compositions as thermoelectric materials, we determined the pertinent parameters—namely, electrical resistivity ρ (Ω cm), Seebeck coefficient S(μV/deg), and thermal conductivity k(watts/cm deg) in order to be able to compute the "Figure of Merit" Z(deg^{-1}) given by $Z = S^2 \cdot \rho^{-1} \cdot k^{-1}$. The samples used for the electrical measurements were bars, ¼ in × ¼ in × 2 in which were either hot-pressed (1000°C, 6000 lb in^{-2}) or cold-pressed and subsequently sintered by inductive heating to between 1000° and 1400°C. Either procedure yielded densities around 90 per cent of theoretical, and all data are characteristic of this condition only, no extrapolation to theoretical densities having been attempted. The d.c. resistivities were determined by a two-point method, using a standard 0.01 Ω resistance, a 2V battery as a power source and a Leeds and Northrup Type K2 potentiometer. Considering sample inhomogeneities, an accuracy of no better than ±5 per cent can be claimed.

The effect of the actual density of the specimen on the electrical resistivity is best demonstrated by the values in Table 2, which were obtained with samples of varying densities.

TABLE 2.—COMPARISON OF ELECTRICAL RESISTIVITIES ON SAMPLES OF DIFFERENT DENSITIES

Composition	ρ, 25°C ($\mu\Omega$ cm)	ρ, 196°C ($\mu\Omega$ cm)	% Density
USi_3	21	5.3	100 (arc-melted ingot)
UGe_3	36	8.6	100 (arc-melted ingot)
USi_3	37	-	79
UGe_3	59		81

The Seebeck coefficient was measured with a Type K2 potentiometer. Thermal e.m.f. was generated by butting the bars between two copper blocks turned from the same piece of stock, one of which was heated by means of a heating tape, the other water-cooled by a coil soldered onto the block. The temperature gradient was measured by means of two thermocouples located in holes drilled to the centre of the bar immediately behind the contact faces. Here again the error is about ±10 per cent. Thermal conductivity for most samples was measured only at room temperature by a technique similar to that described by WEISS[8]. The apparatus consists essentially of a heater, whose input in watts can be accurately determined, the cylindrical sample ($\sim\frac{1}{2}$ in. diameter $\frac{1}{4}$ $\frac{1}{2}$ in. thick) and a heat sink, generally held at room temperature. In order to cut radiation and residual gas conduction losses to a minimum, the whole apparatus is placed inside a silvered vacuum chamber which is held at $\sim 10^{-[illegible]}$ mm Hg. Calculation of k is according to

$$k = \frac{l}{A}\,\frac{Q}{\Delta T}$$

where l is the length of the sample, A the cross-sectional area and Q the heat input. A sample of $AgSbTe_2$ with a reported thermal conductivity of 7.8 mW cm^{-1} deg^{-1} gave values summarized in Table 3. We can see that even with threefold variation in ΔT reproducible results were obtained on this low-conductivity material. With samples of high conductivity, this was not the case and we had to use longer samples with holes drilled from the side to the centre of the cylinder into which the thermocouples were fixed with conductive epoxy resin. This technique yielded reproducible results to 5 per cent.

TABLE 3.—THERMAL CONDUCTIVITY OF $AgSbTe_2$

ΔT across sample (°C)	Thermal conductivity in (mW cm^{-1} deg^{-1})
8.98	7.89
11.66	7.91
38.85	7.78

Thermal conductivity at elevated temperatures was measured for USi_3 only by the technique described by KINGERY[9]. The sample used was a hot-pressed $\frac{3}{4}$ in. diameter cylinder 1 in. long. The test specimen was sandwiched between two standard alumina rods of the same dimensions which were obtained from the Norton Company and had a reported thermal conductivity over the temperature range studied of 0.02 W degree^{-1} cm^{-1}. As soon as the thermal current was established as equal through both standards, the thermal current through the sandwiched unknown, together with the temperature difference, gave the thermal conductivity.

The room temperature data are summarized in Table 4 and Fig. 1 gives the thermoelectric properties of USi_3 as a function of temperature.

In general, we can see that both the electrical resistivity and the Seebeck coefficient for all compositions increase with temperature. The columns marked $\Delta\rho$ and ΔS give the change of these

---

[8] H. WEISS, *Ann. Phys. Lpz.* **4**, 121 (1959).

[9] J. FRANCL and W. D. KINGERY, *J. Amer. Ceram. Soc.* **37**, 80 84 (1954).

TABLE 4. ELECTRICAL PROPERTIES OF SOME USi_xGe_{3-x} COMPOSITIONS AT 25°C

Composition	ρ ($\mu\Omega$ cm)	k (W/cm^{-1} degree^{-1})	$\Delta\rho$ ($\mu\Omega$ cm/°C)	S (μV/°C)	Z (degree^{-1} 10^4)	ΔS (μV/°C)
USi_3	37	0.20	0.095	18	0.44	0.031
$USi_{2}Ge_{0}$	41	0.17	0.11	18	0.47	0.041
$USi_{.0}Ge_{1.0}$	43	0.155	0.12	17	0.43	0.044
$USi_{1.5}Ge_{1}$	51	0.14	0.16	19	0.51	0.058
$USi_{1.0}Ge_{2.0}$	49	0.135	0.13	13	0.26	0.069
$USi_{0}Ge$	53	0.15	0.18	14	0.25	0.070
UGe_3	59	0.18	0.17	12	0.19	0.073

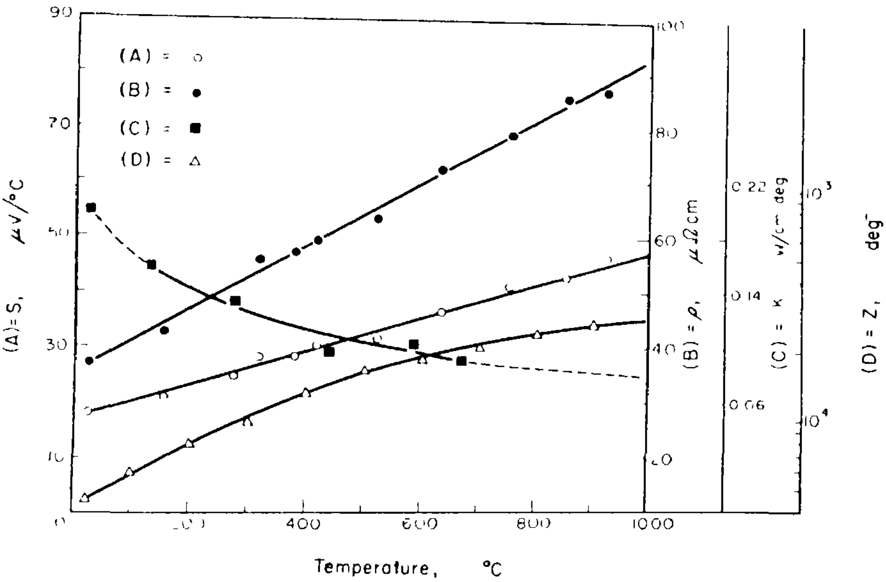


FIG. 1.—Thermoelectric properties of USi_3 as a function of temperature.

properties per °C. The electrical properties have all been measured up to 1000°C and up to this point increase practically linearly with temperature. We can notice that going from straight silicide to straight germanide the increase of both resistivity and Seebeck coefficient becomes steeper. Fig. 1 also includes the thermal conductivity of USi_3 as a function of temperature, and we can see that it varies roughly as $T^{-1/2}$. If we assume the same temperature behaviour for $USi_{1.5}Ge_{1.5}$, taking 0.07 W/cm^{-1} degree^{-1} as thermal conductivity at 1200°C, we can extrapolate a Figure of Merit of 0.5×10^{-3} degree^{-1} which represents probably the top range of quality for these types of materials.

Modifications of USi_3

The rather intriguing simple cubic structure of USi_3, which may be considered an ABO_3-type perovskite structure with the B atom missing (see Fig. 2), offered the possibility of attempting the preparation of some silicide analogs of the type $UMeSi_3$. Using the GOLDSCHMIDT[10] formula for the ideal perovskite, $r_A + r_0 = \sqrt{2}(r_B + r_0)$, we can get an idea on the size atom which may fit the hole in the USi_3 structure. Since we do not know to what degree metals would ionize on entering the USi_3 structure the GOLDSCHMIDT rule was only a rough guide. As atoms, essentially only carbon and boron might fit the hole. The following elements were arc-melted together with the stoichiometric quantities of U and Si to form $UMeSi_3$: Ag, Cr, Fe, C and B. $UCrSi_3$ and $UAgSi_3$ gave

---

[10] V. M. GOLDSCHMIDT, *Geochem. Verteilungsges.* VII (1926), VIII (1928).

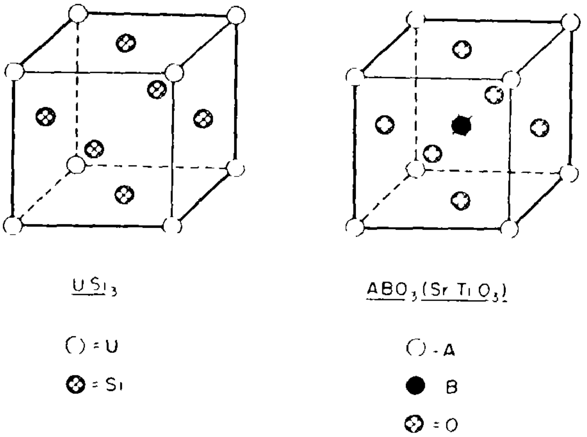


FIG. 2 Comparison of USi_3 and ABO_3 structure

essentially a USi_3 pattern with slightly expanded parameters but did not show any Cr or Ag lines. This might suggest that Cr or Ag form solid solutions with USi_3, substituting for U as well as for Si. In the case of $UFeSi_3$ we obtained some single crystals exhibiting plate-like tetragonal symmetry. The following parameters could be assigned: $a_0 = 4.03$ Å, $c_0 = 48.75$ Å, space group D_{4h}^{19} – $I4/amd$. These data were derived from Laue, rotating crystal and precession photographs. The intended $UCSi_3$ and $UBSi_3$ also gave only the well-known USi_3 pattern. Since no graphite or boron could be detected, these atoms are either in the ½ ½ ½ position of the USi_3 structure or are amorphous to x-rays.

The electrical properties of all these modified compositions were not significantly enough different from those for pure USi_3 to be studied in any detail.

DISCUSSION

The solid solutions of USi_3 and UGe_3 are essentially metallic in nature. Since the arrangement of atoms in the particular UX_3 structure permits a high coordination and hence the opportunity for strong metallic bonding, we have this character reflected in the low electrical resistivity, exhibiting a positive temperature coefficient and the low thermoelectric power. It was, therefore, hoped that the thermal conductivity in the solid solutions could be sufficiently lowered to make these compositions useful as thermoelectrics. The high average atomic weight for USi_3 (80.6) and UGe_3 (113.7) as well as the high metal to nonmetal ratio (8.5 for USi_3) should be in favour of a low thermal conductivity. The data in Table 4 indicated that a reduction of k was achieved by forming solid solutions but the effect was not nearly as significant as has been observed for the Si/Ge system. Calculation of the electronic contribution to the thermal conductivity according to the Wiedeman Franz law indicates that there is very little phonon contribution. Despite the still high thermal conductivity, indications are that at 1200 C a Figure of Merit of 0.5×10^{-3} degree^{-1} might be achieved. Since these materials are thermally quite stable at these temperatures such properties would constitute a significant advantage over the selenides and tellurides present in developments.

Acknowledgements — The author greatly appreciated the cooperation of Dr G TEUFER in getting the single crystal data and the assistance of Mr A J WEISSMANN in obtaining the other lattice parameters.

J Inorg Nucl Chem 1963, Vol 25 pp 789 to 794 Pergamon Press Ltd Printed in Northern Ireland

NUCLEAR MAGNETIC RESONANCE STUDIES IN THE SERIES $ZrF_4\,xHF\,yH_2O$—I

THE CONSTITUTION OF THE HYDRATES OF ZIRCONIUM TETRAFLUORIDE

S Maričić, P Strohal and Z Veksli
' Rudjer Bošković ' Institute, Zagreb, Yugoslavia

(*Received* 27 *December* 1962)

Abstract Proton and fluorine magnetic resonance spectra prove that the hydrates of zirconium tetrafluoride are correctly formulated as $ZrF_4\,H_2O$ and $ZrF_4\,3H_2O$ The results are related to the possible crystal structure of the trihydrate It is found that 10-20 per cent surplus water is unavoidably incorporated into the crystal lattice of the monohydrate prepared by the usual methods, but pure monohydrate could be obtained by dehydrating $ZrF_4\,3H_2O$ at 110 C

VARIOUS compounds of the general composition $ZrF_4\,xHF\,yH_2O$ are of interest in connection with the recovery of uranium reactor fuel elements (alloyed with zirconium), during which the first step is dissolution in hydrofluoric acid Recent investigations(1 2 3) of this series of compounds have focused attention on the structures of the mono- and the tri-hydrate of zirconium tetrafluoride As no complete crystal structure work has yet been published, it seemed worthwhile to obtain additional and independent information regarding the chemical constitution of these two compounds (x 0) The nuclear magnetic resonance method was convenient for this purpose for several reasons

EXPERIMENTAL

Sample preparation

In addition to chemical analysis, both X-ray and NMR techniques were used in characterizing the pure compounds The last technique proved especially useful in discovering admixtures containing hydrogen, which otherwise would not have been detected

$ZrF_4\,H_2O$ was prepared in the following two ways

(i) by dissolving reactor grade zirconium metal in a 1 1 mixture of concentrated nitric acid and 48 per cent hydrofluoric acid as described by CHAPMAN and SLANSKY(4)

(ii) by addition of 90 per cent of the theoretical quantity of a 40 per cent w/w aqueous hydrofluoric acid to zirconium oxychloride with the final acetone treatment as given in the paper of D'EYE *et al* (1)

The final products, after drying to constant weight at 80°C, gave X-ray diagrams characteristic of the monohydrate, according to the literature(1 5) Slight differences in the central part of the NMR spectra were noted, and these are discussed later in connection with the dehydration of the trihydrate to the monohydrate By the first method one obtains a product in the form of coarse crystallites, and a good NMR signal to noise ratio was therefore achieved However the yield was rather better in the second method, so that most of work reported here has been done on such a monohydrate in spite of somewhat poorer NMR signals

---

R W M D'EYE, J P BURDEN and F A HARPER *J Inorg Nucl Chem* **2**, 192 (1956)
R I WELLS, U S A E C Report IDO-14455 (1958)
I N WATERS, *J Inorg Nucl Chem* **15**, 320 (1960)
A G CHAPMAN and C M SLANSKY, U S A E C Report IDO 14442 (1958)
I KOLDITZ and A FELTZ, *Z Anorg Chem* **310**, 217 (1961)

Two methods were also used for $ZrF_4 \cdot 3H_2O$:

(i) either of the two monohydrates, dried at room temperature, was dissolved in 6N nitric acid at 50°C. (It was found necessary to add some hydrofluoric acid in order to obtain a pure product.) After several days, crystals of the trihydrate were formed. This procedure is based on the data of CHAPMAN and SLANSKY[1]

(ii) the second method consists of dissolving zirconium oxide in hydrofluoric acid; the insoluble part was centrifuged off and the liquor evaporated to near dryness. After some time a precipitate forms which is a *mixture of both the mono- and the trihydrate. It is converted to the trihydrate in* several days at room temperature by adding some 1 : 1 nitric acid.

The X-ray diagrams for both samples were identical and in agreement with the data of WATERS[4]. The NMR *spectra were also the same, but as the second method was found somewhat safer, most of* the NMR measurements were done with such samples.

Analytical

The fluorine in the hydrates was estimated by the pyrohydrolytic method and by radiometric titration of fluoride[6] with europium nitrate using ^{152}Eu as a tracer. The results obtained agreed within the experimental error with those from thermogravimetry, measuring at 350°C and 1000°C the weight of $ZrOF_2$ and ZrO_2 respectively. Zirconium was determined gravimetrically as ZrO_2 by precipitation from aqueous solution and heating to 1000°C.

The amount of water was calculated by difference. For the trihydrate the loss of weight at 120°C was also measured.

The results of several analyses are summarized as the ratios

	Zr	F	H_2O
monohydrate	1	3.83	1.19 ± 0.04
trihydrate	1	3.94	2.96 ± 0.03

The high Zr/F ratio is accounted for by the presence of some hafnium in the zirconium used in this work, a point already mentioned by D. FYE *et al.*[1] Obviously, the water content in the trihydrate becomes smaller for this reason, while the result for the monohydrate must be attributed to surplus water.

Apparatus

The NMR spectrometer used was of a conventional bridge-type, with insulation in the probes made of either teflon (for proton resonance) or polythene (for fluorine resonance). The specially constructed sample-containers (see Fig. 1) were filled under anhydrous condition in a dry-box.

RESULTS

The room temperature spectra (absorption first derivatives) of the trihydrate are given in Fig. 2. The signal to noise ratio at lower temperatures was poor,* but no great change in the line shape of proton resonances was noticed as compared with Fig. 2. However, the fluorine resonance showed significant broadening at 213°K both by the line width (*increasing from 7.2 to 9.2 G*) and the second moment value (13.0 gauss^2). These seem to be the same down to liquid air temperature.

The results for the monohydrate are shown in Fig. 3. There are three representative proton resonance lines taken at room temperature, which are (1) due to samples obtained by direct synthesis and dried at 80°C, (2) from such a sample, but heated to constant weight at 200°C, and (3) due to a monohydrate sample prepared by dehydrating the trihydrate at 110°C.

---

* Signals were partially saturated even with an r.f. voltage across the probe of the order of 1 mV.

[6] E. I. ONSTOTT and W. P. ELLIS, *Analyt. Chem.* **28**, 393 (1956).

At 213°K, line No 1 is still the same, but at 77°K it becomes somewhat broader with a shape similar to the line No 3 The fluorine resonances are practically unaffected by temperature

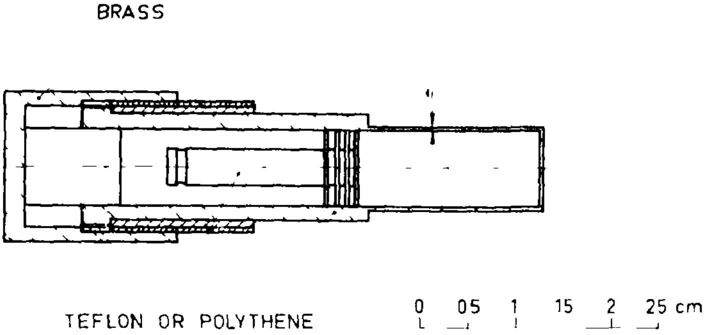


FIG 1 The container for samples in NMR work

DISCUSSION

The main object in discussing the present results is to find the correct chemical constitution for the compounds whose chemical formulae represent them as the mono- and trihydrate of zirconium tetrafluoride Most generally one can have the following combinations

	A	B	C
monohydrate	$ZrF_4\,H_2O$	$ZrOF_2\,2HF$	H_2ZrOF_4
trihydrate	$ZrF_4\,3H_2O$	$ZrOF_2\,2HF\,2H_2O$	$H_2ZrOF_4\,2H_2O$

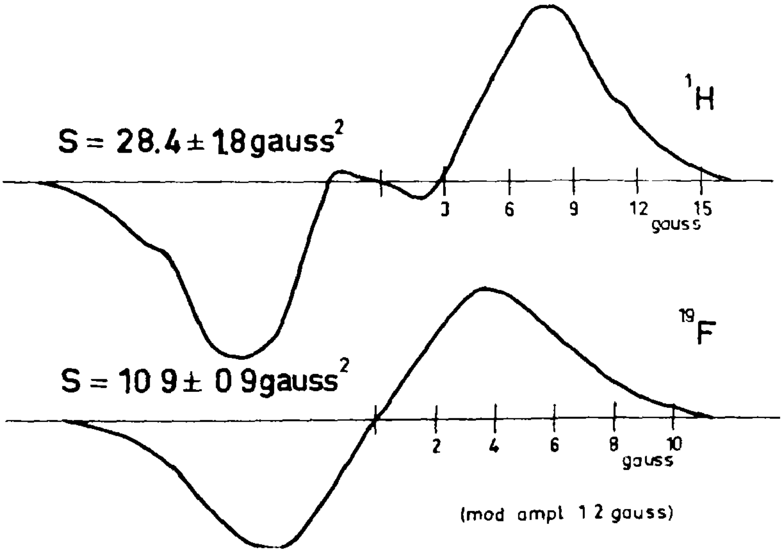


FIG 2 Proton and fluorine magnetic resonance spectra of zirconium tetrafluoride trihydrate at room temperature

Some of these have been suggested in the literature, especially in the earlier papers, but none seems to be established with sufficient certainty KOLDITZ and FELTZ[5] reject for the monohydrate the formulation B and C because infra-red spectra show the deformation band of the water molecule This result is not conclusive owing to the presence of 10 20 per cent incorporated water in monohydrate samples prepared by the methods used to date

We shall discuss later the narrow maximum in the proton resonance line of the monohydrate containing certain surplus of water (cf Fig 3, line 1) We note that all the three proton lines in Fig 3 have the same line width of the broad component,

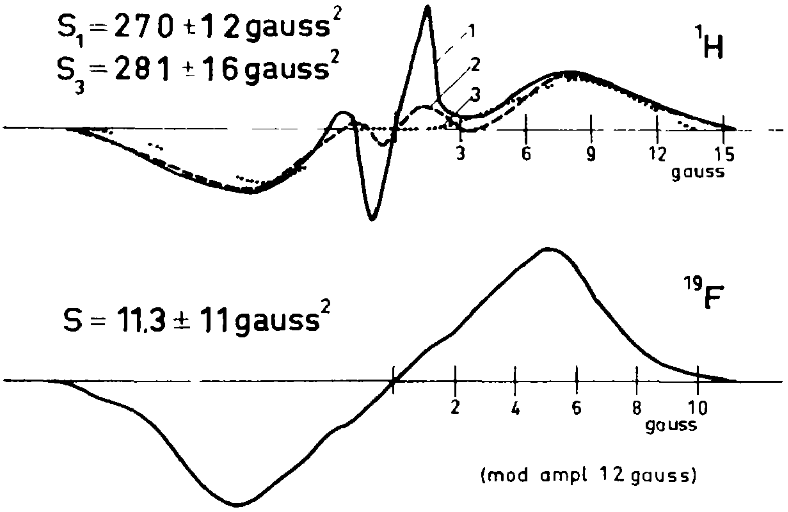


Fig 3 Proton and fluorine magnetic resonance spectra of zirconium tetrafluoride monohydrate at room temperature Proton resonance lines obtained on samples
- - (1) from direct synthesis (dried at 80°C)
(2) same as (1) but heated at 200 C
(3) by dehydrating the trihydrate at 110 C

characteristic of a two-spin line encountered thus far in so many hydrates Our measurements at liquid-air temperature, though not sufficiently accurate for quantitative interpretation, do confirm a two-spin line-shape, identical to the one represented by line 3 in Fig 3 In addition, the second moment values are characteristic of a pair of protons in a water molecule It is therefore certain that in this case the water molecule implied by the formula ZrF_4H_2O is indeed contained as such in the crystal lattice of the monohydrate of zirconium tetrafluoride

Formulations B and C, apart from their unlikeliness from a purely chemical point of view, have to be rejected also because in such a case, the proton resonance should be a single narrow line, certainly much narrower than the observed one for two protons of a water molecule

The same reasoning applies to the trihydrate, with one difference regarding formulations B and C For these, the proton resonance line should be composed, to the first approximation, of a broad component due to protons of water molecules and a narrow one from the more or less isolated protons in either HF (B) or "oxotetrafluorozirconic acid" (C) respectively The ratio of the integrated intensities of the broad to the narrow line should be 2 1 However, the result shown in Fig 2 clearly indicates only the presence of water molecules Owing to a better signal to noise ratio in this case one can distinguish the characteristic details of a two-spin line, i e the shoulders at the "wings" and the central part. Thus, there is clear-cut evidence from proton resonance spectra, that hydrogen in both these crystalline compounds is present only bound in water molecules.

One interesting point is the presence of some 20 per cent excess water in monohydrate samples obtained by direct synthesis. It should be noted that it was present irrespective of the method of preparation, and that X-ray diagrams were always identical and characteristic of the monohydrate phase. The proton resonance spectra showed minor differences in intensities of the narrow component at room temperature. No simple drying up to 130°C caused any diminution of the central peak. However, at higher drying temperatures this peak became smaller, but part was still present even at 200°C (see Fig. 3).

The monohydrate obtained by dehydration at 110°C from the trihydrate had no central narrow peak. All this evidence together with the dehydration experiments of D'Eye *et al.*[1] suggest that surplus water in the monohydrate is not physically adsorbed in the usual sense. As far as proton resonance results go, this water is reorienting quickly, and yet it is quite tightly bound within the crystal lattice. Only by the complete change of the trihydrate crystal structure into that of the monohydrate, or by extreme drying of the monohydrate, can it be avoided. The latter procedure is risky, because Koldiiz and Feltz[5] report that decomposition sets in at 230°C and H_2O evolution is accompanied by HF. Thus, in order to avoid incorporation of surplus water during synthesis, new methods of obtaining a stoichiometrically well-defined monohydrate of zirconium tetrafluoride are desirable.

Various compounds in the present series are of importance for studying the F···H—O hydrogen bond. Data on this kind of hydrogen bond are scanty, and no correlation between infra-red frequency shifts and bond dimensions is as yet possible. There is also great need for crystal structure information. In view of this a full interpretation of the present results must await till at least something about the crystal structures of the compounds is known.

Waters[3] mentions that difficulty in single crystal growing prevent any X-ray crystal analysis of the monohydrate, but that some preliminary results in this respect have been obtained with the trihydrate. While one is compelled to reject his suggestion about the formulation $ZrOF_2 \cdot 2HF$ for the monohydrate in the light of the present results, we shall try to see here how they correlate with his proposal for the crystal structure of the trihydrate.

In this, dimers of trigonal dodecahedra $(ZrO_3F_4)_2$ are held together by hydrogen bonds forming "sheets separated by approximately 4 Å and held together by van der Waal's forces". These dimers are stated to have similar eight-fold co-ordination around Zr atoms as in the crystal structure of K_2ZrF_6.[7] If this is true, then the present results would require the six oxygen atoms of a dimer to be actually water molecules taking part in the eight-fold co-ordination around zirconium. The remaining eight fluorine atoms may be visualized at corners of two distorted tetrahedra, each around one zirconium atom. One would certainly expect more distortion within such a dimeric configuration than within the corresponding section of the structure in reference (7). On the other hand, lacking more definite information about the present case, we made a model of such a dimer with deliberate simplification in that all Zr-F,

H Bode and G Teufer, *Acta Cryst* 9, 929 (1956) and for that matter all Zr OH$_2$ links are the same The value chosen was 2 64 Å, the average value from reference (7) The water molecules were supposed to be at the "free" corners left behind if the bridging in WALLERS' dimer is accepted to be through two fluorine atoms (We take this with some reservation owing to the fact that one does not expect to distinguish by X-rays between oxygen and fluorine atoms easily) After this is done, we are still left with the question of possible orientation of water molecules in respect to the rest of the structure We made calculations of the Van Vleck's second moment sum (of fluorine resonance) for two extreme possibilities, and the results did not differ greatly we obtain 4 43 G^2 for one and 4 04 G^2 for another orientation of the water molecules In both cases the fluorine contribution to this "intramolecular" second moment is, of course, the same 2 82 G^2 The experimental second moment of the fluorine line for the trihydrate at room temperature is 10 9 ± 0 9 G^2 Therefore, there is about 6 7 G^2 to be accounted for by the contribution of the magnetic nuclei in neighbouring dimers, if the assumed interatomic distances in this structure are basically correct

That this is roughly so is supported by the "intermolecular" part of the second moment estimated from proton magnetic resonance Its second moment for the trihydrate at room temperature is 28 4 ± 1 8 G^2 Some librational freedom of water molecules at this temperature should be expected, so that an apparent interproton distance of 1 60 Å is reasonable This requires about 22 G^2 for the intramolecular part of the proton resonance second moment On subtracting from the experimental value, one obtains about 6 4 G^2 for the intermolecular contribution The latter value is in agreement with the one required from the preceding discussion of the fluorine resonance data It is permissible to make such a crude comparison of the two values because of similarity in magnetic moments of the hydrogen and fluorine nucleus The good apparent agreement is anyway fortuitous owing to the canceling effect of the number of "intermolecular" terms, and the corresponding summation constants for the two cases

A similar treatment of the monohydrate data is practically impossible There is a definite change in crystal structure when the trihydrate (triclinic) is transformed into the monohydrate (tetragonal), and yet no drastic change in fluorine resonance spectra appears In such a dehydration two of the three water molecules are removed quite easily A difference in binding between these and the last molecule of water (left in the monohydrate) as required by the present observations should also reflect itself in the distortion of the proposed$^{(3)}$ trigonal dodecahedra of the trihydrate crystal structure In view of the preliminary results at low temperature the monohydrate structure seems to be more at rest than the trihydrate one Whether this is due to the difference in the motion of water molecules, or fluorine atoms, or all of them, remains to be seen Whatever the cause, it does seem that the co-ordinating species around the zirconium atom in the monohydrate phase are more tightly bound, but it is difficult to predict with any certainty what type of co-ordination is in the monohydrate

Acknowledgement—The authors are indebted to Professor D GRDENIĆ for suggesting this line of research and his continuous interest Thanks are due to Mr J TUTA for substantial help in preparing and analyzing the samples We had useful discussions with Dr M RANDIĆ and Dr (Mrs) C DJORDJEVIĆ

J. Inorg. Nucl. Chem. 1963. Vol. 25. pp. 795 to 800. Pergamon Press Ltd. Printed in Northern Ireland

PREPARATION AND PROPERTIES OF SOME URANIUM SELENIDES AND TELLURIDES

L. K. MATSON, J. W. MOODY, R. C. HIMES
Battelle Memorial Institute, Columbus, Ohio

(*Received* 20 *October* 1962; *in revised form* 10 *January* 1963)

Abstract—Selenides and tellurides of uranium have been prepared by solid–vapour reaction and densified by melting. Melting points were estimated and some structures were determined by X-ray analysis. Electrical resistivities, Hall coefficients and thermoelectric powers of specimens of compounds were measured. The electrical properties indicate, generally, that these compounds are semimetallic conductors.

RESEARCH on the uranium selenides and tellurides was undertaken with the objective of developing a systematic body of knowledge on the preparation and properties of these compounds. Seven compounds within the two systems have been described in the literature; however, most of this past work was concerned with structural studies and few chemical- or physical-property data are given. Accordingly, an experimental programme was initiated to develop suitable laboratory-preparation techniques for the compounds and to determine certain of their basic properties. Particular emphasis was directed toward assay of properties of importance in electronics.

The existence of USe, U_2Se_3, USe_2 and a selenide with a higher Se content than USe_2 has been reported in the uranium–selenium system.(1) Uranium diselenide seems to occur in two modifications, while USe was reported to have a NaCl structure.(2)

Four compounds within the uranium–tellurium system have been described. UTe is reported to have NaCl-type structure while U_3Te_4 is isotypic with Th_3P_4. UTe_2 is tetragonal.(2) Uranium sesquitelluride has also been reported.(3)

METHOD OF PREPARATION

The uranium compounds were prepared by reaction of chalcogen vapour with turnings of uranium metal at elevated temperatures. The tellurium employed was C.P. grade (about 99.99 per cent pure) stick tellurium obtained from the Fischer Scientific Co. The selenium was the American Smelting and Refining Company's rectifier-grade selenium shot of about 99.999 per cent purity. The uranium used had only 0.01 per cent spectrographically detectable impurities.

The reactants in selected stoicheiometric proportions were contained in a simple evacuated Vycor capsule (designed as illustrated in Fig. 1). Oxides were removed from the surfaces of the uranium turnings by washing in dilute nitric acid and rinsing with distilled water and then acetone immediately before they were loaded in the capsule. An indentation in the bottom of the reaction tube served to prevent direct contact of the elements in the condensed state (and a possible violent reaction) and assured a smoothly-proceeding solid–vapour reaction.

The reactions were carried out in a resistance-wound tube furnace. The temperature of the furnace was increased gradually until the reaction appeared visually to be complete, when the tubes were inspected on trial withdrawal from the furnace. The temperature was then raised another 100°C and the reactants maintained at this temperature for about 24 hr. Final temperatures of approximately 700 and 875°C were required for the selenides and tellurides, respectively.

---

(1) A. COLANI, *C.R. Acad. Sci., Paris* **137**, 382–383 (1903); *Ann. Chim.* **12**, 85 (1907).

(2) R. FERRO, *Z. Anorg. Chem.* **275**, 320–326 (1954).

(3) A. COLANI, *C.R. Acad. Sci., Paris* **137**, 383 (1903); *Ann. Chim.* **12**, 87 (1907).

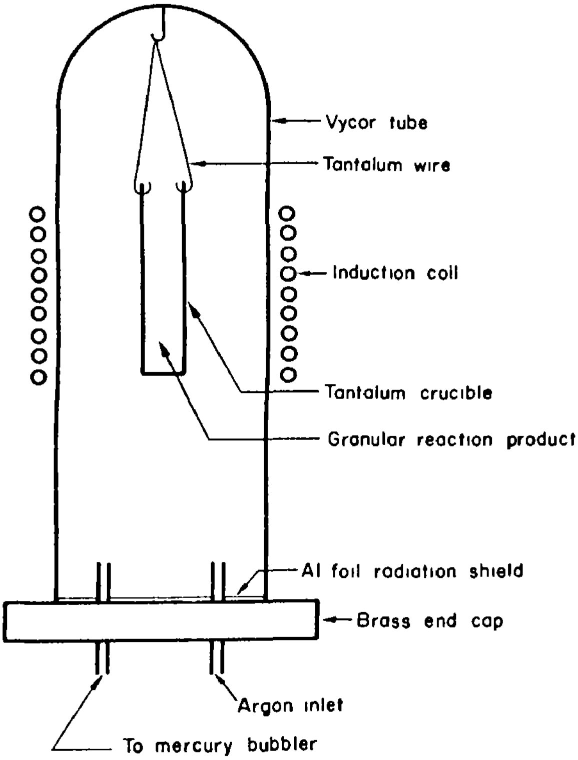


FIG. 1. Apparatus used to densify the uranium chalcogenides.

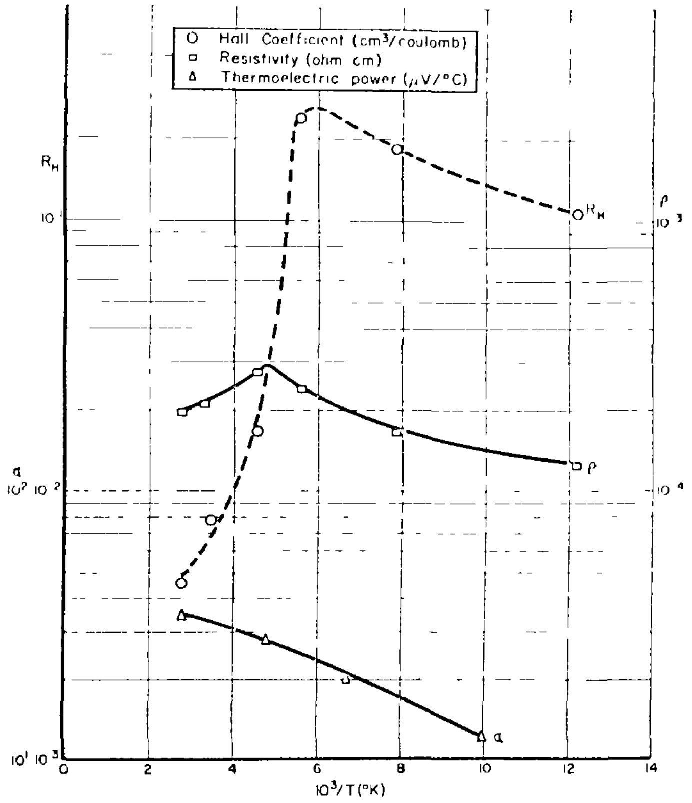


FIG. 2.—Electrical properties of a P-type sample of USe as a function of reciprocal temperature.

In all cases, the reaction products were obtained in a granular form. These products were cast into ingots by melting under argon in a tantalum crucible in the apparatus illustrated in Fig. 1. The tantalum crucible was suspended from a Quartz hook by means of tantalum wire. Power for the induction heating employed was supplied by a 20 kW, Lepel r.f. generator.

It was possible to estimate the melting points of these compounds by noting, as the temperature was increased slowly, (1) the highest temperature at which solid could be observed visually and (2) the lowest temperature at which liquid was definitely observed. This range of temperature which was measured with an optical pyrometer was relatively small in most cases and it is felt that the data give a reasonable estimate of the melting points of the compounds. (Decomposition of the compounds at the melting points appeared to be negligible.) The data are given in Table 1 along with some other physical properties determined in the course of this work. It is interesting to note that the melting points of each series of compounds tend to decrease as the metalloid to metal ratio increases. As would be expected, a given selenide melts at a higher temperature than the corresponding telluride.

TABLE 1.—PHYSICAL PROPERTIES OF URANIUM SELENIDES AND TELLURIDES

Synthetic composition	Melting point (°C)	Crystal structure	Lattice constant (a_0)	Calculated density (g/cm^3)	Determined density (g/cm^3)
USe	1850–2000	NaCl(B-1)	5.71	11.3	10.9$_1$ [11.07 by ref (1)]
U_2Se_3	1560–1590	Weak lines*	–	–	9.4$_3$
USe_2	1350–1380	Weak lines, but different from U_2Se_3	–	–	9.0$_9$
UTe	1550–1650	Th_3P_4 (major phase)	9.393	8.81	
		NaCl (minor phase)	6.151	10.43	9.6$_3$ [10.37 by ref (3)]
U_3Te_4	1430–1470	Th_3P_4	9.3980 [9.397 by ref (2)]	9.81	9.4$_6$
U_2Te_3	1325–1355	Th_3P_4	9.3960	9.18	9.0$_2$
UTe_2	1215–1235	Single phase but complex†	—	—	8.9$_1$

* An orthorhombic structure of Sb_2S_3 type (a = 11.33, b = 10.94, and c = 4.06) was reported$^{(1)}$.

† A tetragonal structure (a = 4.006, c/a = 1.865) which is neither of CaC_2 or Cu_2Sb type was reported$^{(3)}$.

To establish conditions suitable for handling the compounds, a few simple tests were made to determine their reactivity with common reagents and atmospheres. With but few exceptions, the selenides and tellurides of uranium react readily with both acids and bases. With acids, hydrogen selenide or hydrogen telluride is generated. However, UTe_2 does not appear to react with concentrated hydrochloric acid. Neither USe nor U_2Se_3 was found to react with 3 N KOH.

Except for UTe_2, the uranium telluride samples disintegrated in air in a matter of days. The uranium selenides do not show this tendency. (A surface reaction occurred at 300°C on USe.)

CRYSTAL STRUCTURES

A limited X-ray analysis of the various compositions was undertaken as a proof of preparation. In some cases, the powder diagrams could not be indexed with great accuracy and in one case (UTe) the preparation proved to be polyphase. Thus, the symbolic representation used in designating the materials prepared indicates the nominal composition of the material but does not necessarily indicate that the material is a single-phase specimen of a compound having precisely the denoted stoicheiometry.

The results of the X-ray data are summarized in Table 1. The uranium monoselenide (USe) preparation was found to have the B-1 type (NaCl) structure as reported in the literature. The structure of the sesqui- and diselenide compositions could not be definitely determined. However, it was established that the X-ray patterns were dissimilar, which indicates the presence of different phases at the two stoicheiometries

The uranium telluride sample of over-all one-to-one composition was found to consist of a major phase with a Th_3P_4 structure and a minor phase with a NaCl structure. A Th_3P_4 structure was found for both U_3Te_4 and U_2Te_3. It will be noticed that the lattice constant of U_3Te_4 was larger than that for the Th_3P_4-structured phases of either the one-to-one composition or the two-to-three composition. Thus, it appears that vacancies occurring in either the cation or anion sublattice of the Th_3P_4 structure of these latter phases lead to a decrease in the lattice constant.

Uranium ditelluride was found to be single phase but it was not possible to index the complex X-ray pattern obtained for this composition. The USe ingot proved to be a large single crystal as cast.

Densities of all the preparations were determined by comparing their weights in air and in carbon tetrachloride. These measured densities are given in Table 1 where they may be compared with theoretical densities of the compounds as calculated (when possible) from their unit-cell dimensions. It will be noted that the measured density of the UTe composition is intermediate between that calculated for the two structures found even though the Th_3P_4 structure was the dominant phase found by X-ray analysis.

ELECTRICAL PROPERTIES

The samples prepared here were not subject to extensive purification or crystallization procedures and, thus, they were not in that condition of refinement and crystalline perfection generally desirable for studies of the electrical properties of materials. Even so, it was felt that a study of the electrical properties of these preparations might yield important information on the bonding in the compounds and provide guidance for future studies. Samples for electrical measurement were taken from the densified ingots. These samples were fashioned into small parallelepipeds onto which electrical leads were soldered with indium metal. Electrical resistivity, Hall coefficient, and thermoelectric power were measured at various temperatures. (Unfortunately, the tellurides disintegrated before their thermoelectric powers could be determined.) Representative data, obtained at room temperature and liquid nitrogen temperature, are given in Table 2. All the compounds studied had rather high charge-carrier concentrations as evidenced by the low Hall coefficients. Carrier concentrations,

TABLE 2.—ELECTRICAL PROPERTIES OF SOME URANIUM SELENIDES AND TELLURIDES

Synthetic composition	Temperature (°K)	Resistivity (ohm-cm)	Hall coefficient (cm^3/coulomb)	Thermoelectric power (μ-v/°K)
USe	300	2.8×10^{-4}	+0.008	+38
	80	1.2×10^{-4}	+0.12	+21
U_2Se_3	300	2.3×10^{-3}	−0.009	2
USe_2	300	3.34×10^{-2}	+0.01	+21
	80	5.7×10^{-1}		
UTe	300	1.3×10^{-3}		
	80	1.2×10^{-3}	+0.2	
U_2Te_3	300	5.5×10^{-3}	+0.02	
	80	7.0×10^{-3}	+0.31	
UTe_2	300	1.2×10^{-2}		
	80	1.0×10^{-2}	−0.34	

calculated from the Hall coefficients, ranged from about 2×10^{19} to about 10^{21} carriers/cm^3 The very low values of the Hall coefficient preclude ascribing much precision to the values quoted, however, it is felt by the authors that the relative magnitudes are correct and meaningful The signs of the Hall coefficient and thermoelectric power (where measured) were positive for all samples except U_2Se_3 and UTe_3 Electrons appeared to be the dominant charge carriers in U_2Se_3 and UTe_2 The high carrier concentrations found immediately suggest that these compounds are semimetallic conductors

The electrical properties of the single crystal of USe are of particular interest At room temperature, the thermoelectric evaluation factor (*ZK*, equal to thermoelectric power squared divided by the resistivity) is $5\ 6 \times 10^{-6}$ watt per cm-deg This is higher than for the other compounds studied and may be compared with an evaluation factor of about 3×10^{-5} for *p*-type Bi_2Te_3 at room-temperature At high temperatures, the thermoelectric properties of USe may compare even more favourably with the best known thermoelectric materials The mobility of the charge carriers, as calculated from the product of the Hall coefficient and conductivity, is encouragingly high for such an unrefined material Because of this, the electrical properties of USe were investigated in greater detail In Fig 2 are shown the Hall coefficient, resistivity and thermoelectric power as functions of reciprocal temperature The general character of the curves shown have been confirmed by measurements on other specimens It will be noted that the thermoelectric power is increasing in a region where the Hall coefficient is decreasing The behaviour of the electrical properties of the sample over the temperature range of the measurements is consistent with semimetallic conduction and the notion of overlapping bands At higher temperatures, the resistivity of the sample increased to a second maximum Such behaviour is suggestive of some phase transition but much more data would be necessary to resolve this question

It was of interest to determine the effects of stoicheiometric deviations on the electrical properties of USe Two additional samples were prepared from nominal compositions containing one atomic per cent excess uranium and one atomic per cent excess selenium, respectively These changes had no significant effect on the electrical properties of the compound It is interesting to note, however, that electrons, rather than holes, were the dominant carriers in the U_2Se_3 sample

The dominant charge carriers in USe are holes, as evidenced by the positive Hall coefficients and thermoelectric powers of the samples One may speculate that, if the bonding in the compound were predominantly ionic, then *n*-type (electron) conduction might be expected, since uranium has more valence electrons than are needed formally, to satisfy the Se^{2-} ion Thus, it appears that any suitable model of the conduction processes in USe must attribute importance to covalent bonds

Since the arrangement of atoms in the rock-salt structure involves octahedral coordination, the covalent bonds of selenium might be expected to be of the p^3d^2s hybrid type involving the 5*s*-orbital, since the 4*s*-orbital is at so much lower energy Such hybridization is found in $[SeBr_6]^{2-}$ (4) The covalent bonds of uranium would probably be of the f^3d^2s type (as, for example in the compound UCl_6), since the alternate structure, d^2sp^3, requires promotion of three pairs of electrons from the 5*f* to the 7*p* shell (5)

---

(4) L Pauling, *The Nature of the Chemical Bond* pp 184–185, Cornell University Press (1948)

(5) J C Eisenstein, *J Chem Phys* **25**, 143–146 (1956)

[illegible] covalent bonding does operate, each uranium [illegible] would [illegible] electrons to the bonding system. Each selenium atom would contribute [illegible] four electrons, holding an inert pair in the 4s-orbital. Twelve electrons would be needed to fill the six octahedral bonds to one atom in USe, and the proposed bonding system lacks two electrons. Thus, it seems reasonable to hypothesize that the p-type conductivity observed for USe is due to unsatisfied bonds. That the bonds are strongly covalent was also concluded by KHODADAD[6] on the basis of oxidation studies of USe, U_3Se_4 and U_2Se_3 with Hg^{2+} ions. On the basis of these considerations, one might postulate that PuSe would be a semiconductor should it exist in the rock salt structure. Plutonium has two more electrons than does uranium which could be contributed to the bonding system.

Acknowledgement—The authors wish to thank the Selenium and Tellurium Development Committee whose sponsorship made this work possible and Dr. D. A. VAUGHN who performed the X-ray analyses. Helpful discussions with Messrs. J. F. MILLER and R. T. BATE are also acknowledged.

[6] P. KHODADAD, *C.R. Acad. Sci., Paris* **253**, 1575–1577 (1961).

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 801 to 805. Pergamon Press Ltd. Printed in Northern Ireland

SOME ADDUCTS OF PHOSPHINES AND AMINES WITH BORANE

P. A. CHOPARD and R. F. HUDSON
Cyanamid European Research Institute, 91 route de la Capite
Cologny-Geneva, Switzerland

(*Received* 23 *October* 1962, *in revised form* 16 *January* 1963)

Abstract—Toluene is readily liberated from tribenzyl methyl and triphenyl benzyl phosphonium borohydrides, which were found to be very resistant to further pyrolysis. In contrast, the adduct of tribenzylamine and borane dissociates before decomposition. N-Dibenzyl borazane gave the *monomeric* borazene at 150, whereas N-benzyl borazane gave the anticipated trimeric borazine.

THE adducts which are readily formed from diborane and amines or phosphines may in some cases be prepared⁽¹⁾ by the action of lithium borohydride on the corresponding amine or phosphine hydrochloride, e.g.

$$\mathrm{R_1R_2R_3\overset{+}{N}H + BH_4^- \rightarrow R_1R_2R_3N \rightarrow BH_3 + H_2}$$

Recently HEAL⁽²⁾ has shown that P-tetraphenyl borohydride decomposes at 200 *in vacuo* to give benzene and triphenylborophane in 50 per cent yield

$$\mathrm{Ph_4P^+BH_4^- \rightarrow Ph_3P \rightarrow BH_3 + C_6H_6}$$

and similar reactions have been observed with certain ammonium and sulphonium derivatives.⁽³⁾

We find that quaternary phosphonium borohydrides containing one or more benzyl groups decompose readily, owing to stabilization of the benzyl group by conjugation. Thus triphenyl benzyl phosphonium borohydride loses toluene almost quantitatively in boiling chloroform, and a similar reaction also occurs when tribenzyl methyl phosphonium bromide is boiled with sodium borohydride in diglyme.

$$\mathrm{Bz\overset{+}{P}h_3BH_4^-} \xrightarrow{60^\circ} \mathrm{Ph_3P \rightarrow BH_3 + Ph-Me}$$

$$\mathrm{Bz_3\overset{+}{P}MeBH_4^-} \xrightarrow{150} \mathrm{Bz_2PMe \rightarrow BH_3 + Ph-Me}$$

The addition compounds formed from diborane and primary or secondary amines normally decompose with the liberation of hydrogen.⁽⁴⁾ Thus primary amines usually give the borazines⁽⁵,⁶⁾ directly because of the high conjugation energy of the cyclic

---

(1) G. W. SCHAEFFER, and E. R. ANDERSON, *J. Amer. Chem. Soc.* **71**, 2143 (1949). H. NOTH and H. BEYER, *Ber.*, **93**, 928 (1960).

(2) H. G. HEAL, *J. Inorg. Nucl. Chem.* **16**, 208 (1961).

(3) H. G. HEAL, *J. Inorg. Nucl. Chem.* **12**, 255 (1960).

(4) M. F. LAPPERT, *Chem. Rev.* **56**, 959 (1956). J. C. SHELDON and B. C. SMITH *Quart. Rev.* **14**, 200 (1960).

(5) W. V. HOUGH, G. W. SCHAEFFER, M. DZURUS and A. C. STEWART *J. Amer. Chem. Soc.* **77**, 864 (1955).

(6) (a) G. W. SCHAEFFER, R. SCHAEFFER and H. I. SCHLESINGER *J. Amer. Chem. Soc.* **73**, 1612 (1951).

(b) H. J. BECHER and S. FRICK *Z. Anorg. Chem.* **295**, 83 (1958).

(c) E. WIBERG and K. HERTWIG, *Z. Anorg. Chem.* **255**, 141 (1947).

system, and we have obtained trimeric N-benzyl borazine directly from benzylamine and diborane (see p 804)

$$3\,Bz\quad NH_2\quad 1\tfrac{1}{2}B_2H_6 \rightarrow (BzN\,BH)_3 + 6H_2$$

Phosphines however give borophenes,(7) because of the relatively weak multiple bonding in phosphorus compounds

$$RPH_2 \rightarrow BH_3 \rightarrow (RPH\quad BH_2)_n + H_2$$

Secondary amines(6) and phosphines(8) similarly give cyclic or polymeric derivatives, viz ,

$$Me_2NH \rightarrow BH_3 \xrightarrow{H_2} (Me_2N\quad BH_2)_2$$

$$R_2PH \rightarrow BH_3 \xrightarrow{H_2} (R_2P\quad BH_2)_n$$

In view of the lability of the benzyl group in the phosphonium borohydrides described above we have investigated the pyrolysis of some benzyl substituted boranes

N-Dibenzyl borazane decomposed at 150°/10 12 mm to give the corresponding monomeric N-dibenzyl borazene but no toluene

$$Bz_2NH \rightarrow BH_3 \rightarrow Bz_2N\quad BH_2 + H_2$$

The stability of the monomeric form in this case is attributed to steric hindrance of the benzyl groups which prevents further association This borene, unlike the known dimeric forms,(1, 6) reacts violently with hydroxylic solvents, and even with acetone, but pyrolysis of this product did not give the borazine A small quantity of toluene (corresponding to ca 20 per cent of one equivalent) was however obtained at high temperatures

Tribenzyl borazane dissociated on heating to 100 150° without giving the corresponding borazene

$$Bz_3N \rightarrow BH_3 \rightarrow Bz_3N + \tfrac{1}{2}B_2H_6$$

In contrast, P-dibenzyl methyl borophane was found to be extremely stable thermally, and was recovered unchanged after heating to 200° for long periods, even in the presence of an excess of lithium aluminium hydride HEWITT and HOLLIDAY(9) have however detected a small quantity of methane, in addition to the dissociation products, on the pyrolysis of $Me_3P \rightarrow BH_3$

These results show that a hydrogen atom of the quaternary group is necessary for the further decomposition of the borazanes to borazenes and borazines This suggests that the decomposition proceeds by the reaction of an incipient proton, at the BH_3 group, as follows,

$$R_2NH \rightarrow BH_3\quad [R_2N - BH_3]^- H^+ \rightarrow R_2N\quad BH_2 + H_2$$

rather than by the nucleophilic attack of an incipient hydride ion on a hydrogen atom or alkyl group of the quaternary atom,

$$R_2NH\quad BH_3 \not\rightarrow R_2\overset{+}{N}H - BH_2 + H^-$$

If this were the case, the benzyl borazenes mentioned above would decompose further

---

(7) R I WAGNER and F F CASERIO, *J Inorg Nucl Chem* **11**, 259 (1959)

(8) A B BURG, *Angew Chem* **72**, 183 (1960)

(9) F HEWITT and A K HOLLIDAY, *J Chem Soc* 530 (1953)

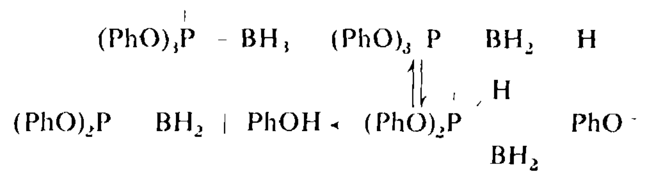
Moreover the first mechanism is supported by the decomposition of the trimethylborane adducts(10) as follows,

$$H_3N \rightarrow BMe_3 \xrightarrow{200} CH_4 + H_2N\ \ BMe_2 \rightarrow CH_4 + (HNBMe)_3$$

$$PhNH_2 \rightarrow BMe_3 \rightarrow CH_4 + PhNH - BMe_2 \rightarrow CH_4 + (PhN\ \ BMe)_3$$

which are difficult to explain in terms of the second mechanism

The incipient hydride ion may however displace a highly labile group from the quaternary phosphonium centre Thus triphenoxy borophane readily gave one equivalent of phenol and a polymeric phosphorus compound Since we have shown(11) that the displacement of phenol from quasi-phosphonium salts is extremely facile, the following mechanism may be proposed



$$(PhO)_3\overset{+}{P} - BH_3 \quad (PhO)_3P\ \ BH_2\ \ H$$
$$\rightleftharpoons$$
$$(PhO)_2P\ \ BH_2 + PhOH \leftarrow (PhO)_2\overset{H}{\underset{BH_2}{P}}\ \ PhO^-$$

According to this mechanism, nucleophilic displacement on phosphorus by an incipient hydride ion of a phenoxide ion, is followed by the removal of the hydrogen atom of the phosphonium intermediate in the form of a proton by the basic phenoxide ion

EXPERIMENTAL

*Reaction of sodium borohydride with triphenyl benzylphosphonium bromide**

A solution of 0 8 g (0 021 mole) of sodium borohydride in 60 ml of dry diglyme was added to 7 g of the phosphonium salt (0 016 mole) in 200 ml of dry chloroform The precipitated sodium bromide was filtered off, after 10–15 min The chloroform was then boiled off under reduced pressure to give a colourless crystalline product (2 7 g 45 per cent) m p 295-300 (Found C 79 9, H, 7 19 P 7 86 Calc for $C_{25}H_{26}BP$ C, 81 5, H, 7 26 P, 8 42 per cent) The infra-red spectrum showed a characteristic B–H peak at 2220 cm $^{-1}$

The remaining diglyme-chloroform solution was heated to 50–60 for 2 hr under reduced pressure and then diluted with about three volumes of water to precipitate 1 2 g (27 per cent) of white crystals, m p 170–180 (Found C, 77 8, H, 6 89 P, 11 0 Calc for $C_{18}H_{18}BP$ C, 78 2, H, 6 82 P 11 2 per cent) The B-H peak (infra-red) was observed at 2380 cm $^{-1}$ This product was identical with the authentic sample of triphenyl borophane prepared from triphenylphosphine and diborane m p 180-182

In a further experiment, about 30 per cent of one equivalent of toluene was detected by v p c in the diglyme-chloroform solution The borophane was also obtained in comparable yields when the above borohydride was heated at 130–140 /0 1–0 2 mm, or when it was boiled under reflux overnight in a mixture of chloroform and hexane

Reaction of sodium borohydride with tribenzyl methyl phosphonium bromide(12)

Ten grammes of tribenzyl methyl phosphonium bromide (0 025 mole) were boiled overnight in diglyme with 2 g of sodium borohydride (0 053 mole) After filtration of the NaBr over Celite', the filtrate was treated with water to give 5 6 g of white needles m p 132 (from ethanol) (Found C 74 7, H, 8 15, P, 13 4 Calc $C_{15}H_{20}BP$, C, 74 2, H, 8 30, P, 12 8 per cent) Mol Wt 224 (Calc 242)

When P–dibenzylmethyl borophane was heated for 2 hr at 200 under reduced pressure (15 mm) no visible decomposition took place, and the m p was unaltered However, the recovered material had a strong phosphine-like odour, indicating slight thermal dissociation. When the product was heated overnight to 180–200° in triglyme with ten equivalents of lithium aluminium hydride, most of the starting material was recovered after treatment with water.

---

* Prepared from triphenylphosphine and benzyl bromide in benzene

(10) E Wiberg, K Herwig and A Bolz, *Z Anorg Chem* **256,** 177 (1948) **257,** 138 (1948), H J Becher, *Ibid* **289,** 262 (1957)

(11) R F Hudson and P A Chopard, *Helv Chim Acta* **45,** 1137 (1962)

(12) W J Bailey and S A Buckler, *J Amer Chem Soc* **79,** 3567 (1957)

Reaction of diborane with dibenzylamine

Diborane(14) generated from 8.4 g of $NaBH_4$ (0.22 mole) in 100 ml of diglyme, and 64.3 g of $BF_3 \cdot Et_2O$ (0.44 mole) in 100 ml of diglyme, was bubbled at room temperature into a solution of 30 g of dibenzylamine (0.15 mole) in 100 ml diglyme, over a period of 1 hr. The solution was then evaporated under reduced pressure below 100° and 24 g of white crystals were collected m.p. 94–95°. (Found: C, 79.9; H, 8.64; N, 6.42. Calc. for $C_{14}H_{18}BN$: C, 79.7; H, 8.53; N, 6.64 per cent.) The infrared spectrum showed one peak at 3200 cm^{-1} (N–H) and three peaks at 2280, 2300 and 2390 cm^{-1} (B–H region).

The above product (50 g) was heated under nitrogen at reduced pressure. Gas evolution started at 100°/15 mm and was violent at 150°. A colourless substance (25 g) which solidified in the receiver, distilled at 110–112°/0.05 mm, m.p. 96–97° (from monoglyme). (Found: C, 78.56, 79.3; H, 7.76; N, 6.29, 6.24. Calc. for $C_{14}H_{16}BN$: C, 80.0; H, 7.65; N, 6.67 per cent. Mol. Wt. 250 (Calc. 209).)

The infra-red spectrum had no peak in the N–H region, and two peaks between 2400 and 2500 cm^{-1}. The product reacted violently with ethanol, giving benzylamine (identified by means of its hydrochloride); it reacted also with acetone but the product was not identified. Trimeric or dimeric borazenes have been reported to be inert under these conditions.(8c)

On further distillation, 6 g of a viscous liquid, b.p. 180–182°/0.2 mm, were collected. The products of two different runs gave the following analyses (Found: C, 82.37, 79.45; H, 7.31, 7.58; N, 5.53, 6.56 per cent. Mol. Wt. 222, 235). The infra-red spectrum showed one peak at 2450 cm^{-1}. This product was not investigated further. The undistillable residue, approximately 15 g was dissolved in warm monoglyme (40–50 ml). The cold solution deposited a white waxy solid, soluble in alcohol, combustible in air but which when heated to redness in the absence of air did not melt, but slowly darkened to give finally a hard black powder (probably boron nitride). Reproducible analyses of the white solid could not be obtained by conventional methods, although the molecular weight of 460, measured isopiestically, was reproducible. The infra-red spectrum showed no B–H peak, but gave a weak absorption at 3300 cm^{-1}. There was also an intense absorption in the 1300–1400 cm^{-1} region (B–N),(11) and the peaks characteristic of aromatic monosubstitution of benzylamine were still present in the 700–800 cm^{-1} region. Calculated boron content for BzBN (C_7H_7BN) is 9.5 per cent (observed B = 9.12 per cent). (When Me_2NBH_2 was pyrolysed $(Me_2N)_2BH$ and $Me_2N \cdot B_2H_5$ were obtained(15).)

In another experiment, the borazene (22.5 g) was heated to 300° at atmospheric pressure for 1.5 hr. Two grammes of toluene (about 20 per cent of one equivalent) were collected.

Reaction of diborane with benzylamine

Diborane, from $NaBH_4$ (0.8 mole) and $BF_3 \cdot Et_2O$ (1.6 mole), was bubbled into a solution of benzylamine (57.5 g, 0.5 mole) in diglyme (200 ml). The solvent was evaporated under reduced pressure at 60–70° to give 55 g of a white deliquescent solid m.p. 45–50°. Part of this material was heated to 280° and then distilled at 180–182°/0.005 mm without further decomposition. (Found: C, 71.0; H, 6.90; N, 11.6. Calc. for $C_{21}H_{21}B_3N_3$: C, 72.0; H, 6.75; N, 12.0 per cent. Mol. Wt. = 330. Calc. for $(BzN–BH)_3$ = 350.) The infra-red spectrum showed no N–H peak, but a peak at 2480 cm^{-1}, and strong absorption in the 1400 cm^{-1} region. There was also a band at 725 cm^{-1} (this region is considered to be characteristic of the borazene ring,(16) but in the present case, its origin is doubtful since the C–H out of plane vibration of the benzylamine ring absorbs in the same region).

Reaction of diborane with tribenzylamine

Tribenzylamine (30 g, 1.05 mole) was treated with an excess of diborane in diglyme as previously described. Twenty-four grammes (75 per cent) of the expected adduct, which was insoluble in most common solvents, were collected. (Found: C, 83.5; H, 8.20; N, 4.26. Calc. for $C_{21}H_{24}BN$: C, 83.7;

---

(13) H. C. Brown and B. C. Subba Rao, *J. Amer. Chem. Soc.* **81**, 6428 (1959).

(14) D. W. Aubrey, M. F. Lappert and H. Pyszora, *J. Chem. Soc.* 5239 (1960).

(15) A. B. Burg and C. L. Randolph, *J. Amer. Chem. Soc.* **73**, 953 (1951).

(16) D. W. Aubrey, M. F. Lappert and H. Pyszora, *J. Chem. Soc.*, 1931 (1961).

7 97, N, 4 65 per cent) This adduct dissociated completely at ca 240 in a sealed tube When it is boiled overnight in diglyme (160), tribenzylamine only was left in the solution In a test tube, the adduct dissociated into its components at 100 , and the liberated borane ignited explosively

Reaction of borane with triphenyl phosphite

Freshly distilled triphenyl phosphite (62 g, 0 2 mole) b p 140–142 /0 01 mm, in monoglyme (200 ml) was treated with diborane prepared from $NaBH_4$ (0 3 mole) and BF_3Et_2O (0 6 mole) After removal of the solvent under reduced pressure, 49 g of white crystals of P-triphenoxy borophane were collected, yield 75 per cent m p 46–48° (from petroleum ether) (Found C, 66 0, H, 5 49, P, 9 31 Calc for $C_{18}H_{18}BPO_3$ C, 66 7, H, 5 56, P, 9 56 per cent) The infra-red spectrum showed a strong peak at 2400 cm^{-1}

This solid (6 6 g) was heated to 130–140 in triglyme (20 ml) to give an amorphous solid which precipitated from the solution The mixture was boiled for 4 hr, and the filtrate found to contain 80 per cent of one equivalent of phenol, by comparing the infra-red spectrum with those of solutions of phenol of known concentration

Acknowledgement -We thank Dr J PELLON of the Central Research Division, American Cyanamid, Stamford, Connecticut for making the isopiestic molecular weight determinations Mr G SALVADORI for technical assistance, and Dr M GREEN for valuable discussions

J Inorg Nucl Chem 1963 Vol 25 pp 807 to 818 Pergamon Press Ltd Printed in Northern Ireland

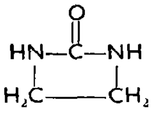
METAL ION COMPLEXES OF 2-IMIDAZOLIDINONE (ETHYLENE UREA)

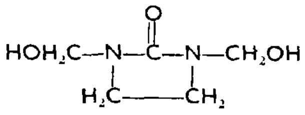
R J Berni,* R R Benerito,† W M Ayres‡ and H B Jonassen§

(*Received* 1 *October* 1962, *in revised form* 16 *November* 1962)

Abstract—Complexes of ethylene urea (2-imidazolidinone), with the metal ions Zn(II), Cd(II), Cu(II), Fe(III), and Co(II), have been prepared Infra-red spectra and differential thermograms of ethylene urea and all five complexes have been analysed X-ray powder diffraction data, reflectance spectra and magnetic susceptibilities have been obtained

N-methylol compounds have become important in imparting crease resistant properties to cotton and other textiles Ethylene urea (abbreviated EU) is the starting material in the syntheses of the most widely used of these N-methylol compounds, dimethylolethylene urea (abbreviated DMEU)


EU


DMEU

Recent studies by Ziifle *et al* [1,2] on the mechanism of the catalysis of the DMEU-cellulose reaction have indicated complex compound formation between the metal ion catalyst and DMEU Since complexes of substituted ureas have not been investigated extensively, it became of interest to verify the existence and to study properties of these and related metal ion complexes using ethylene urea as the ligand

Ethylene urea is a neutral, colourless and odourless solid which melts at 131° The compound was first prepared in 1886[3] and recent patents and publications[4,5] have described commercial preparation in high yields Physical properties have been determined previously [6]

EXPERIMENTAL

Purification of ethylene urea

Commercial EU of 95 per cent purity was obtained from Metro-Atlantic, Inc , Centredale, Rhode Island It was distilled and recrystallized from ethanol or chloroform m p 130 131° (Found N, 32 23 Calc for $C_3H_6N_2O$ N, 32 54)

---

* Department of Chemistry, Tulane University, New Orleans, La Abstracted in part from the M S Thesis of Ralph J Berni, Tulane University, 1961 Presented before the Division of Inorganic Chemistry at the 1962 Southwest Regional Meeting of the American Chemical Society, Dallas, Texas, December 6–8, 1962

† United States Department of Agriculture, Southern Regional Research Laboratory, New Orleans, La

‡ Chemistry Division, U S Naval Ordnance Test Station, China Lake, California

§ Department of Chemistry, Tulane University, New Orleans, La

(1) H M Ziifle, R J Berni and R R Benerito, *Tex Res J*, **31**, 349 (1961)

(2) H M Ziifle, R J Berni and R R Benerito, *J Appl Polymer Sci* In press

(3) E Fischer and H Koch, *Ann Chem* **232**, 222 (1886)

(4) J F Mulvaney and R L Evans, *Industr Engng Chem* **40**, 393 (1948)

(5) C E Schweitzer, *J Org Chem* **15**, 475 (1950)

(6) K Hofmann, *Imidazole and Its Derivatives* Interscience New York (1953)

Preparation of anhydrous salts and EU complexes

(a) Anhydrous $CuCl_2$, $CoCl_2$ and $FeCl_3$ were prepared from the hydrated salts obtained from Baker Chemical Company by refluxing in thionyl chloride and then distilling under pressure in a nitrogen atmosphere.(7) Anhydrous $CdCl_2$ and $ZnCl_2$ were reagent grade and were used as obtained.

Saturated solutions of EU in absolute ethanol were filtered and mixed with filtered, saturated, ethanolic solutions of the anhydrous metal chlorides. The following conditions were necessary for the precipitation of the complexes: the cadmium complex precipitated overnight at room temperature, the zinc and copper complexes overnight at 4°, the cobalt complex after 2–3 days at 10°, and the iron complex formed overnight at 10°.

(b) *Ethylene urea cadmium (II) chloride* ($2C_3H_6N_2O \cdot CdCl_2$). White crystalline powder, m.p. 262–265°. (Found: Cd, 31.02; Cl, 19.35; N, 15.64; C, 20.38; H, 3.39. Calc. for $C_6H_{12}N_4O_2 \cdot CdCl_2$: Cd, 31.61; Cl, 19.95; N, 15.76; C, 20.27; H, 3.40%.)

(c) *Ethylene urea zinc (II) chloride* ($2C_3H_6N_2O \cdot ZnCl_2$). Colourless crystals, m.p. 188–189°. (Found: Zn, 20.86; Cl, 22.60; N, 18.03; C, 23.50; H, 3.81. Calc. for $C_6H_{12}N_4O_2 \cdot ZnCl_2$: Zn, 21.19; Cl, 22.99; N, 18.17; C, 23.36; H, 3.92%.)

(d) *Ethylene urea copper (II) chloride* ($2C_3H_6N_2O \cdot CuCl_2$). Light green crystals, m.p. 144–145° with decomposition. (Found: Cu, 20.31; N, 18.17; C, 24.00; H, 4.02. Calc. for $C_6H_{12}N_4O_2 \cdot CuCl_2$: Cu, 20.72; N, 18.27; C, 23.50; H, 3.94%.)

(e) *Ethylene urea cobalt (II) chloride* ($3C_3H_6N_2O \cdot CoCl_2$). Dark blue crystals, m.p. 160–161°. (Found: Co, 15.0; Cl, 18.28; N, 21.55; C, 27.95; H, 4.55. Calc. for $C_9H_{18}N_6O_3 \cdot CoCl_2$: Co, 15.18; Cl, 18.27; N, 21.66; C, 27.85; H, 4.67%.)

(f) *Ethylene urea iron (III) chloride* ($2C_3H_6N_2O \cdot FeCl_3$). Orange–brown crystals, m.p. 181–182°. (Found: Fe, 16.76; Cl, 31.41; N, 16.69; C, 21.72; H, 3.68. Calc. for $C_6H_{12}N_4O_2 \cdot FeCl_3$: Fe, 16.70; Cl, 31.81; N, 16.76; C, 21.55; H, 3.62%.)

Instrumental analyses

(a) Infra-red absorption spectra of EU and its complexes were obtained on a Perkin-Elmer Double Beam Spectrophotometer (Model 21) by the KBr disc technique.(8) Nujol mulls of the Cu(II), Cd(II), and Zn(II) complexes were also used for a few infrared spectra analyses.

(b) X-ray powder diffraction curves were determined by the method of Hull-Debye-Scherrer.(9, 10) The instrument employed was a General Electric Company Model XRD-5DF with an SPG spectrogoniometer attached for direct measurement of interatomic spacings.

(c) Magnetic susceptibility measurements were made with a Gouy balance. The apparatus consisted of a Christian Becker analytical balance equipped with an optical system for direct scale reading and a permanent magnetron magnet having a constant field of 4678 G.(11)

(d) Reflectance spectra were obtained in the crystalline complexes with a Beckman DU Spectrophotometer having a 2580 diffuse reflectance attachment. Magnesium carbonate was used as a reference, and the angle of reflectance was 45°.

(e) Differential thermal studies were obtained by use of an apparatus similar to that described by Ayres and Bens.(12) Differential thermograms and gas profiles were however recorded on a Leeds and Northrup Speedomax GX_1-X_2 recorder for ease in interpretation and correlation of data. Glass beads (approximately 0.1 mm in diameter) obtained from the Minnesota Mining and Manufacturing Company were used as sample diluent and inert reference material. Oil-pumped helium, passed through a filter and over hot copper wool prior to entry into the system, was the inert sweeping gas. One gramme of beads was inserted into the sample and reference cells. An accurately weighed amount (approximately 50 mg) of sample was inserted into the sample cell and thoroughly mixed with the beads. The apparatus was assembled, inserted into the heating block, and the gas train connected. Approximately 15 min was allowed for the system to come to equilibrium before the run commenced.

---

(7) A. R. Pray, *Inorg. Syn.* **5**, 153 (1957).

(8) M. M. Stimson and M. J. O'Donnell, *J. Amer. Chem. Soc.* **74**, 1805 (1952).

(9) A. W. Hull, *Phys. Rev.* **10**, 661 (1917).

(10) P. Debye and P. Scherrer, *Z. Phys.* **17**, 277 (1916).

(11) E. Boudreaux, Master's Thesis, Tulane University (1959).

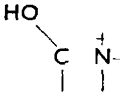
(12) W. M. Ayres and E. M. Bens, *Analyt. Chem.* **33**, 568 (1961).

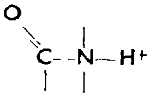
In all runs, the temperature of the gas exit train and thermal conductivity detector was held at 80°C The gas flow rate was approximately 25 ml per min The heating rate over the temperature range of interest 0-400°C) was 6°C per min

RESULTS AND DISCUSSION

Infra-red spectra

Amides may protonate the carbonyl oxygen or the amine nitrogen atoms as shown below in structures I and II


I


II

Resonance considerations favour structure I, and nuclear magnetic resonance studies present evidence that amides protonate the carbonyl oxygen (13) Other authors(14,15) however have presented evidence that protonation of the amido nitrogen is more probable

Since urea acts as a simple amide in many of its reactions, protonation of urea may occur at the carbonyl oxygen or amide nitrogen Metal ions too may form complexes with the urea molecules at either of these two positions Penland *et al* (16) studied shifts in characteristic absorption frequencies in the infra-red region to determine the position of the bonds formed when certain metal ions complex with urea

In the present study, spectra of ethylene urea and five of its metal ion complexes were obtained by use of KBr disk techniques Table 1 includes absorption frequency assignments made by Mecke (17,18) in his study of the infra-red and Raman spectra of ethylene urea and ethylene thiourea Most of the assignments were analogous to those made by Zihli for DMFU crystals

Differences in the spectra of the metal chloride complexes of EU as compared to the EU spectrum occurred at frequencies characteristic of the carbonyl stretching, NH stretching, NH rocking and NH bending vibrations These characteristic absorption bands were checked with spectra obtained by use of Nujol mull techniques

Analysis of spectral curves showed a broadening of the original amide I band of EU in the Co(II) and Cu(II) complexes There was no broadening of this band for the Cd(II) complex Only in the complexes of Zn(II) and Fe(III) was there a resolution of the amide I band into a strong doublet, as indicated in Table 2

These observations are indicative of metal to oxygen bonding in all complexes except that of Cd(II) Only in the Zn(II) and Fe(III) complexes were the metal to carbonyl oxygen bondings of sufficient strength to resolve the amide I band into its components The amide I band(17) has been postulated to be due to a mixed skeletal vibration of OCN and carbonyl Any coordination of metal to carbonyl oxygen would cause some dissymmetry and would lead to a broadening of this band or possible resolution into its

---

(13) G Fraenkel and C Franconi, *J Amer Chem Soc* **82**, 4478 (1960)

(14) J T Edward, H S Chang, K Yates and R Stewart, *Canad J Chem* **38**, 1518 (1960)

(15) M Davies and L Hopkins, *Trans Faraday Soc* **53**, 1563 (1957)

(16) R B Penland, S Mizushima, C Curran and J V Quagliano *J Amer Chem Soc* **79**, 1575 (1957)

(17) R Mecke, Jr, Rei Mecke, Sr and I Luttringhaus, *Ber Ges Dtsch Chem* **90**, 975 (1957)

(18) R Mecke Jr and Rei Mecke Sr, *Ber Ges Dtsch Chem* **89**, 343 (1956)

TABLE 1—INFRA-RED SPECTRUM OF ETHYLENE UREA 3–25 μ REGION KBr DISK

Frequency (cm⁻¹)	Description	Assignments[17, 18]
3279	*m*	NH stretching
2941	*w*	CH_2 in phase stretching
2882	*w*	CH_2 out of phase stretching
1660	*s*	C=O stretching and amide I
1502	*m*	NH bending amide II
1484	*w*	CH_2 symmetrical bending
1445	*m*	CH_2 unsymmetrical bending
1274	*s*	NH unsymmetrical stretching amide III
1101	*m*	NH unsymmetrical stretching
1034	*w*	NH symmetrical stretching
986	*w*	CH_2 out of plane rocking
767	*w*	NH out of plane stretching
700	*wb*	NH rocking
514	*w*	Unassigned

w Weak band
m Medium band
s Strong band
wb Wide band

TABLE 2—OBSERVED INFRA-RED ABSORPTION FREQUENCIES (cm⁻¹) FOR ETHYLENE UREA METAL ION COMPLEXES—KBr DISK

$ZnCl_2 \cdot 2EU$	$CuCl_2 \cdot 2EU$	$FeCl_3 \cdot 2EU$	$CoCl_2 \cdot 3EU$	$CdCl_2 \cdot 2EU$
3367 (*s*)	3311 (*s*)	3356 (*s*)	3322 (*s*)	3450 (*s*)
				3325 (*s*)
2985 (*w*)	2950 (*w*)	2959 (*w*)	2950 (*w*)	2950 (*w*)
2907 (*w*)	2882 (*w*)	2882 (*w*)	2882 (*w*)	2874 (*w*)
1658 (*s*)	1639 (*s*)	1684 (*s*)	1658 (*s*)	1675 (*s*)
1626 (*s*)	1522 (*w*)	1629 (*s*)	1508 (*s*)	1495 (*m*)
1517 (*s*)	1495 (*w*)	1520 (*m*)	1462 (*m*)	1274 (*s*)
1471 (*m*)	1471 (*w*)	1462 (*w*)	1399 (*w*)	1096 (*w*)
1395 (*m*)	1397 (*m*)	1389 (*m*)	1280 (*s*)	766 (*w*)
1282 (*s*)	1282 (*s*)	1282 (*s*)	1096 (*m*)	722 (*w*)
1096 (*m*)	1101 (*m*)	1203 (*w*)	1027 (*w*)	
1021 (*m*)	1028 (*w*)	1015 (*w*)	928 (*w*)	
930 (*m*)	927 (*w*)	746 (*sh*)	761 (*m*)	
750 (*m*)	746 (*sh*)	731 (*m*)	725 (*m*)	
733 (*m*)	734 (*s*)			

(*s*) — Strong band
(*m*) — Medium band
(*w*) — Weak band
(*sh*) = Shoulder

components, with the OCN contribution at higher frequencies than the carbonyl frequencies For these reasons, the absorption bands at 1626 and 1629 cm^{-1} were selected as the carbonyl stretching frequencies and the bands at 1658 and 1684 cm^{-1} were selected as the skeletal OCN contributions for the Zn(II) and Fe(II) complexes respectively Shifts in the 6μ region to longer wave lengths are expected for the following reasons the formation of a metal to oxygen bond (a) increases the electron demand of the donor oxygen and (b) favours the contributing resonance structure depicting increased CN double bond character, The band at 1502 cm^{-1} in EU is assigned by MECKE[17] to the NH bending vibration A shift in this band in the Zn(II) complex to 1517 cm^{-1} and in the Fe(III) complex to 1520 cm^{-1} is in the expected direction of increased CN double bond character and increased bending frequency Also, as a result of the formation of oxygen to metal bond, the 1274 cm^{-1} absorption peak in EU, assigned to the NH unsymmetrical stretching, or amide III band, is shifted to a slightly higher frequency (about 1282 cm^{-1}) for all these complexes except that of Cd(II)

The N-H rocking vibration is also affected by changes in the metal ion of the complex In the instances of the Zn(II) and Fe(III) complexes, increases of 33 and 31 cm^{-1} respectively in the frequency to 733 and 731 cm^{-1} are observed The influence of the metal ion on the rocking vibrations of the ring changes the broad band at approximately 700 cm^{-1} to a sharp peak The magnitude of the shifts at this position of the spectra varied with the metal ion A summary of the shifts in characteristic frequencies with changes in the metal ion appear in Table 3

TABLE 3 -OBSERVED CHANGES IN INFRARED ABSORPTION FREQUENCIES

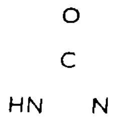
Compound	Amide I		Amide II		N-H rocking	
	Frequency (cm^{-1})	Δcm^{-1}	Frequency (cm^{-1})	Δcm^{-1}	Frequency (cm^{-1})	Δcm^{-1}
Ethylene urea (EU)	1660	–	1502	—	700*	—
$CuCl_2$ 2EU	1639	21	1522	20	734	+34
$FeCl_3$ 2EU	1629	31	1520	18	731	+31
$ZnCl_2$ 2EU	1626	34	1517	15	733	+33
$CdCl_2$ 2EU	1675	15	1495	7	722	22
$CoCl_2$ 3EU	1658	2	1508	6	725	25

* Wide band extended over broad range The band became sharpened into a distinct peak for all the complexes

Similar shifts in the characteristic infra-red bands of the Cu(II) complex are indicative of metal bonding through the carbonyl oxygen

With the Co(II) complex the shifts in the bands characteristic of the amide I and amide II are quite small However, there is a fairly large shift (25 cm^{-1}) in the NH rocking vibration

The infra-red shifts in the Cd(II) complex could possibly be interpreted as indicative of bonding through the NH group, since the carbonyl oxygen stretching is shifted to higher frequency (+15 cm^{-1}) However such coordination should produce large shifts in the NH stretching region which are not observed An important observation, however, is the decrease in the broadening of the amide I band, it is even sharper than in EU This may possibly indicate that the bonding to Cd(II) is through the π cloud the resonating



grouping This would be more in line with crystallographic data recently reported CAVALCA and NARDELLI[19-22] have found through X-ray single crystal analyses that all Cd(II)-urea derivatives studied thus far contain cadmium to oxygen bonding However, MARTINETTE *et al*[23] interpreted changes in the infra-red spectrum of the N-methyl-acetamide-Cd(II) complex as indicative of nitrogen to metal bonding KURODA *et al*[24] also interpreted shifts of the carbonyl frequency as indicative of types of bonding in metal-oxamide complexes X-ray single crystal data on the Cd(II)-EU complex will be obtained and analysed before absolute assignment of the bonding can be made

Based on changes in frequencies of the amide I band, and considering atomic weights of the metals, the order of decreasing stabilities of EU complexes formed by metal through oxygen bonds is

$$\mathrm{Zn(II)} \simeq \mathrm{Fe(III)} > \mathrm{Cu(II)} > \mathrm{Co(II)}$$

From absolute values of frequency shifts, it might be inferred that the stability of the Cd(II) complex of EU is less than that of the Cu(II) complex However, the order of decreasing stability is not necessarily the order of changes in frequency

The characteristic N-H rocking vibration appears as a broad band in EU, in which it would have more rocking freedom than in the EU complex of a metal ion Formation of a complex through the carbonyl oxygen should result in an increase in carbon to nitrogen double bond character in the ring Such a double bond character would result in a sharper peak at higher frequencies as is observed in these complexes

X-ray diffraction

Diffraction curves showed little similarity among the five complexes and indicated the crystals are not isomorphous[25] No attempts were made to use the data to determine the unit cell dimensions The three principal interplanar spacings in order of their relative intensities for ethylene urea and the five complexes are recorded in Table 4

Magnetic susceptibilities

Table 5 presents the magnetic susceptibility data as obtained by the Gouy method $\mathrm{FeCl_3 \, 2EU}$ has a normal moment for Fe(III) of five unpaired electrons and lends support to the evidence that the iron complex is of the outer orbital type

---

[19] L CAVALCA, M NARDELLI and L COGHI, *Nuovo Cimento* **6**, 278 (1957)

[20] L CAVALCA, M NARDELLI and L COGHI, *Gazz Chim Ital* **87**, 903 (1957)

[21] M NARDELLI, L CAVALCA and G FAVA, *Gazz Chim Ital* **87**, 1232 (1957).

[22] M NARDELLI and L COGHI, *Ricerca Sci* **28**, 379 (1958)

[23] B V M MARTINETTE, S MIZUSHIMA and J V QUAGLIANO, *Spectrochim Acta*, 77 (1959)

[24] Y KURODA, M RATO and K SONE, *Bull Chem Soc Japan*, **34**, 877 (1961)

[25] R H HOLM and F A COTTON, *J Phys Chem* **65**, 321 (1961)

TABLE 4 -PRINCIPAL INTERPLANAR SPACINGS FOR EU AND EU COMPLEXES DETERMINED BY X-RAY POWDER DIFFRACTION

Compound	d^1	d^2	d^3
EU	3 85	4 01	2 28
$ZnCl_2$ 2EU	7 21	4 30	3 83
$CdCl_2$ 2EU	7 39	8 45	4 65
$CuCl_2$ 2EU	7 69	4 29	3 71
$CoCl_2$ 3EU	6 60	6 75	4 02
$FeCl_3$ 2EU	4 48	5 62	3 91

d^1, d^2, d^3 = the three principal interplanar spacings (Å) in order of their relative intensities

TABLE 5 — MAGNETIC SUSCEPTIBILITIES OF $FeCl_3$ 2EU, $CoCl_2$ 3EU AND $CuCl_2$ 2EU

Complex	$\Delta W_{s(mg)}$	$M_{s(gm)}$	$\mu_{(Bohr\ magnetons)}$
$FeCl_3$ 2EU	69 0	1 8471	5 91
$CoCl_2$ 3EU	31 3	1 8218	4 35
$CuCl_2$ 2EU	7 75	2 0149	1 89

ΔW_s – the change in weight of the sample upon application of the magnetic field

M_s weight of the sample employed in absence of magnetic field

$CoCl_2$ 3EU has an abnormally high moment for three unpaired electrons, however, Co(II) complexes are known to contain a high orbital contribution (26)

The magnetic criterion is of little help in elucidating the structure of Cu(II) complexes, since the Cu(II) ion has one unpaired electron regardless of the configuration of the bonds $CuCl_2$ 2EU was found to have a moment of 1 89 Bohr magnetons possibly indicating a distorted planar configuration for the complex with the chlorides and carbonyl oxygens at the four corners of the square This would be somewhat analogous to the configuration in the $CuCl_2$–urea complex However, the possibility of an octahedral structure such as in $CuCl_2$ $2H_2O$ must not be overlooked

Differential thermal analysis (DTA)

Gas profile and DTA data for EU and the five complexes up to 320° C are recorded in Table 6 The first thermal change is endothermic for all complexes The order of stability for these complexes as indicated by the onset of the first endothermic peak is

$$\text{Zn(II)} > \text{Fe(III)} > \text{Co(II)} > \text{Cu(II)} \quad \text{Cd(II)}$$

With the exception of the Cu(II) complex, this is the same order of stability as that discussed in the section on infra-red spectra The Cu(II) complex seems to be out of line, possibly because it is the only complex having an exotherm in this region (149 C) All other thermal changes were endothermic with the exception of the second peak for Co(II) at 320°C

---

(26) P W SELWOOD, *Magnetochemistry*, (2nd Ed p 225) Interscience, New York (1956)

TABLE 6 – DTA AND GAS PROFILE DATA UP TO 320°C

Substance	Temperature of onset of thermal reactions (°C) 1st	2nd	3rd	Temperature of onset of gas evolution (°C)
EU	69 endo	113 endo	185 endo	180
$ZnCl_2$ 2EU	176 endo	274 endo		260
$FeCl_3$ 2EU*	158 endo	261 endo		160
$CoCl_2$ 3EU	142 endo	320 exo		280
$CdCl_2$ 2EU	135 endo	256 endo		135
$CuCl_2$ 2EU	136 endo	149 exo	260 endo	120

* Absorbed water liberated at 96°C

The Zn(II) complex shows continuous gas evolution starting at 260°C The Fe(III) complex starts decomposing at 160°C An earlier endotherm observed between 96° and 115°C for Fe(III) complex was shown by gas phase chromatographic techniques to be adsorbed water Its gas profile is extremely complex, possibly indicating an oxidation-reduction Analysis of decomposition products by gas phase chromatographic techniques showed them to be very complex mixtures The complexity of the gas profile may indicate that the two EU molecules are not equivalent in the Fe(III) complex

The unusual composition of the $CoCl_2$ 3EU made it of interest to see if one or more of the EU molecules are solvates Gas evolution was not observed with this complex until 280°C Since this was 100° above the temperature where EU showed an appreciable gas pressure, no EU solvate molecules are indicated

The least stable of the complexes is the Cd(II) complex which shows continuous gas evolution starting at 135°C

The most complex DTA and gas profile curves were obtained from the Cu(II) complex Its gas profile showed five peaks and its DTA curve showed three endotherms and two exotherms in the range up to 400°C Work is underway on identification of the decomposition products and the correlation of endotherms and exotherms to the structure of the complexes

Reflectance spectra

Figs 1, 2 and 3 show reflectance spectra of the three coloured complexes Co(II), Cu(II), and Fe(III), respectively $FeCl_3$ 2EU showed a reflectance band at wavelengths below 500 mμ but none in other regions of the visible spectra $CuCl_2$ 2EU showed a reflectance band at approximately 900 mμ and another below 400 mμ $CoCl_2$ 3EU showed maximum absorption at about 680 mμ, and another absorption at 525 mμ

GENERAL CONCLUSIONS

1 *The* $CuCl_2$ 2EU *complex*

Infra-red data indicate strong metal to oxygen bonding in this complex Such interaction can be explained if skewed octahedral bonding is assumed in this solid complex with d_2sp_3 hybridization In most copper complexes containing ligands with C—O bond, the splitting is such that the $^{d}x^{2}-y^{2}$ orbital is singly occupied whereas the

$^{d}z^{2}$ orbital is filled. The singly occupied $^{d}x^{2}$-y^{2} orbital containing effectively a positive hole should thus have a greater tendency to co-ordinate with the highly electronegative groups of the ligands, as the oxygen of the carbonyl group ($\overset{\|}{\underset{|}{C}}$ –O) of

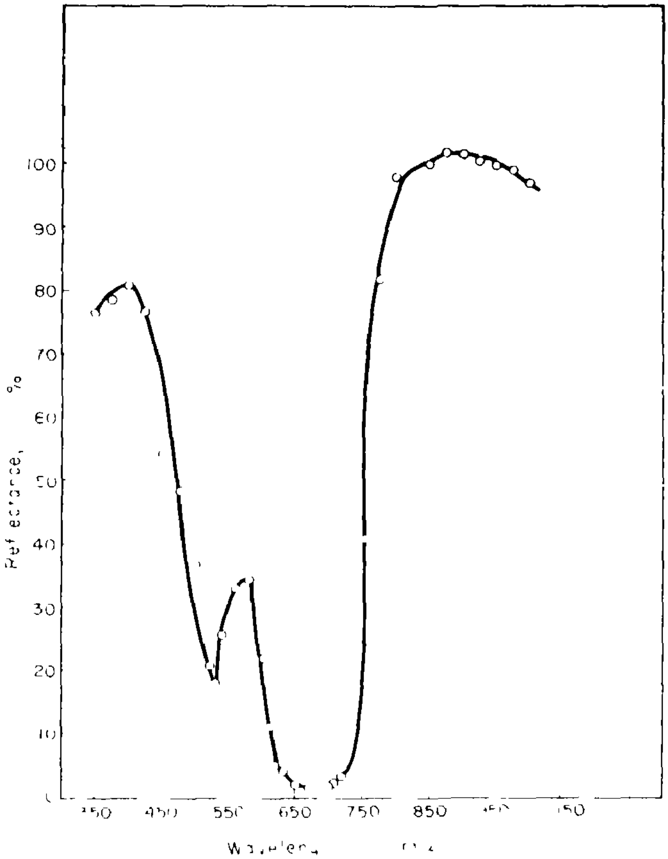


Fig. 1.—Reflectance spectrum of $CoCl_2$ 3EU.

the EU molecule and two chloride ions. Two more chloride ions could occupy the two octahedral positions such as in $CuCl_2$ $2H_2O$.[27] Such bonding explains the observed shifts of the carbonyl stretching of lower frequency and of the NH rocking band to higher frequency. A somewhat skewed octahedral arrangement might be expected to give a magnetic moment slightly higher than the spin only moment.

2. *The* $ZnCl_2$ 2EU *complex*

X-ray powder diffraction data indicate that the Zn(II) and the Cu(II) complexes are not isomorphous. As in most four co-ordinated Zn(II) complexes tetrahedral coordination seems to be achieved through a sigma bond with two Cl ions and two C—O^{-} groups. DTA and infra-red data indicate that this complex is the most stable of the complexes under investigation.

---

(27) L. E. Orgel, *An Introduction to Transition Metal Chemistry*, p. 60. Wiley, New York, Methuen, London (1960).

3 *The* $CoCl_2$ 3EU *complex*

The composition of this complex indicates five co-ordination The magnetic moment (4 3 B M) is too low for octahedral coordination,[28] it also shows that the ligand field is weak and that a high spin complex is formed The reflectance spectrum also is not consistent with six co-ordinated Co(II) The DTA data indicate that all three EU molecules are coordinated The three unpaired electrons occupy the d_{z^2}, $d_{x^2-y^2}$, and d_{xy} orbitals if a trigonal bipyramidal structure is formed Some repulsion should exist in the direction of the ligands producing lengthened metal-ligand distances which are indicated in the small shift of the carbonyl stretching band The filled d_{xz} and d_{yz} orbitals are available for π-bonding and may stabilize the bonding to the Co(II) ion

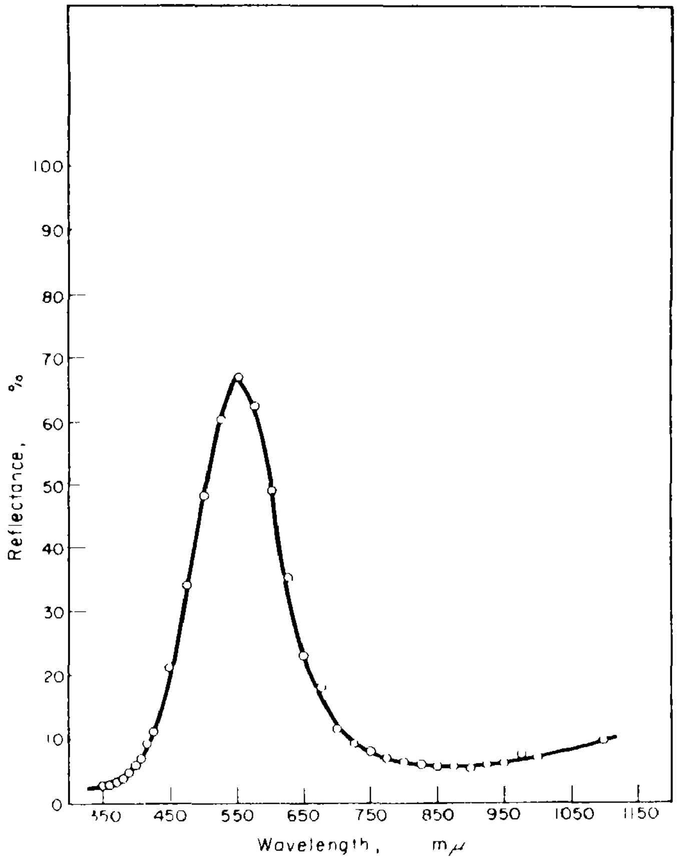


FIG 2 —Reflectance spectrum of $CuCl_2$ 2EU

4 *The* $FeCl_3$ 2EU *complex*

The magnetic moment of this complex shows five unpaired electrons indicating a weak ligand field A five co-ordinated complex, possibly trigonal bipyramidal, seems to be present However, DTA data indicate a somewhat unstable complex with gas evolution starting at 160°C This may possibly indicate that the two EU molecules are

---

(28) M Goodgame and F A Cotton, *J Phys Chem* **65**, 791 (1961)

not equivalent although an oxidation-reduction reaction could be an alternate possibility Stabilization due to π-bonding seems to be less than in the Co(II) complex

5 *The* $CdCl_2$ 2EU *complex*

This complex seems to involve a different type of co-ordination than those previously discussed Its infra-red spectrum indicates a small shift to higher frequency for the carbonyl stretching frequency and to lower frequency for the NH bending mode No large shift of the NH stretching frequency to lower frequency is observed such as was observed by PENLAND(16) for the Pt(II)-urea complex where a shift of more than 100 cm^{-1} to lower NH stretching frequency is observed for the co-ordinated NH_2 group. However, a shift to higher frequency and formation of a doublet is observed (3325 and 3450 cm^{-1}) for the complex (compared to 3279 cm^{-1} for EU) This may indicate that in the Cd(II) complex EU acts as a bidentate ligand with two different NH stretching vibrations Co-ordination through the π system between the oxygen and one of the N donor atoms, stabilized by π bond back donation from the metal ion, could explain the shift to higher frequencies for both the carbonyl and NH stretching modes

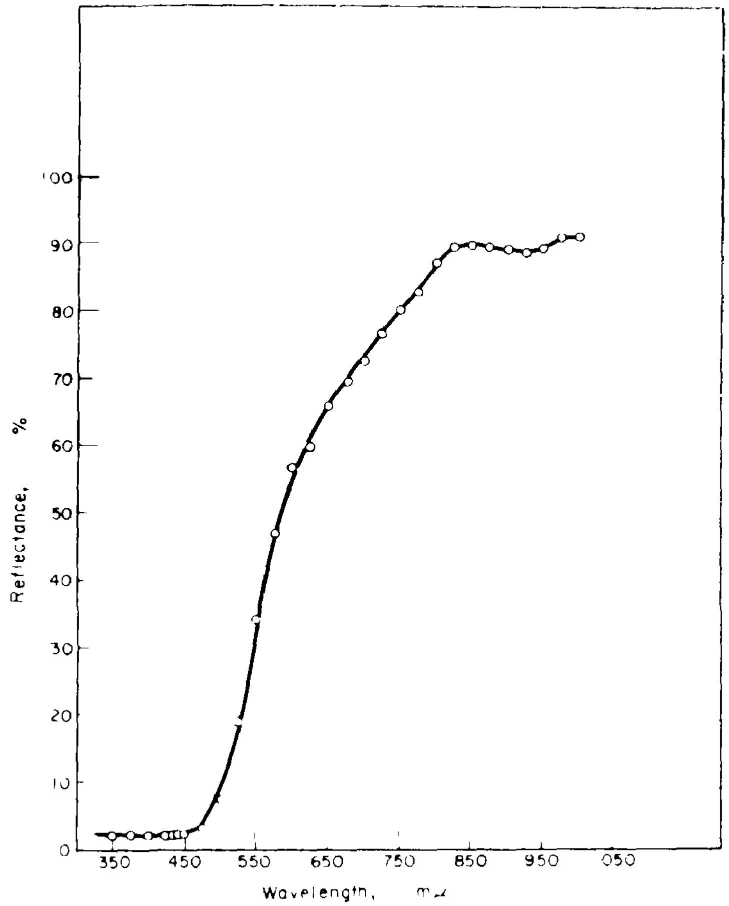
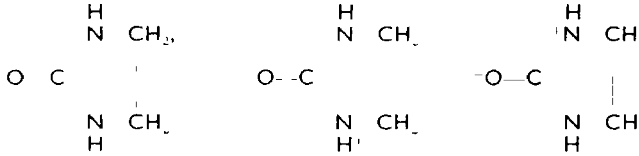


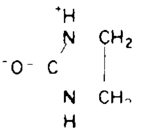
FIG. 3 – Reflectance spectrum of $FeCl_3$ 2EU

6 *The EU molecule*

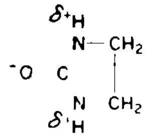
The EU molecule as the urea molecule is postulated to be a resonance hybrid of the following canonical structures



This study seems to indicate that when co-ordinating to certain metal ions, the EU molecule can delocalize its π-cloud over the $O\;\overset{\overset{H}{N}}{\underset{\underset{H}{N}}{C}}$ system to give the following structures



or even



Because of co-ordination with the metal ion, the π-cloud might be spread over three or possibly even four atom systems The specificity of metal co-ordination will determine the amount of electron delocalization in the π-system Preferred co-ordination through the carbonyl oxygen will produce a shift in the carbonyl stretching band to shorter frequencies and an increase in the NH vibration modes In these complexes the EU molecule can then be considered a monodentate group in which the delocalized π-cloud system becomes unsymmetrically disturbed This seems to be the case in all complexes except that of Cd(II), which seems to be symmetrical because of its larger radius of co-ordination Both the carbonyl and NH stretching modes increase in frequency indicating possibly a symmetric co-ordination through both ends of the π-system

Acknowledgements -The help of the following is gratefully acknowledged Dr E BOUDREAUX, Tulane University, for magnetic susceptibility measurements, Messrs L BROWN, D MITCHAM and G BOUDREAUX of the Southern Regional Research Laboratory for elemental analyses, X-ray diffractograms and infra-red spectrographs, respectively

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 819 to 822. Pergamon Press Ltd. Printed in Northern Ireland

COMPLEXES OF THE RARE EARTHS—V

PIPERIDINE-2,6-DICARBOXYLIC ACID

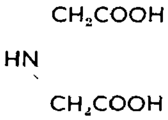
L. C. THOMPSON
Department of Chemistry, University of Minnesota, Duluth, Duluth 12, Minnesota

(*Received* 12 *December* 1962)

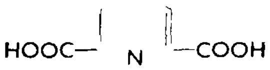
Abstract—Step-wise formation constants have been determined for the rare earths (including yttrium) with piperdine-2,6-dicarboxylic acid. The measurements have been made in aqueous solutions of ionic strength $\mu = 0.1$ (KNO_3) and a temperature of 25°C. The data have been interpreted in terms of 1:1 and 2:1 chelates. Trends in the values of log K_1 and log K_2 are discussed and compared with similar values for other ligands which contain the same basic chelating structure. It is shown that the size of the metal ion is an important factor in determining the magnitude of the formation constants of piperidine-2,6-dicarboxylic acid chelates in much the same way as in the chelates of dipicolinic acid.

AT the present time we have underway in this laboratory a general programme concerned with elucidating the factors which influence the co-ordination of ligands to the rare-earth ions. Of particular interest in this study is the measurement of formation constants for chelates of the rare earths with ligands for which comparable data are available for other metal ions. In this way, it is hoped that comparisons can be made and conclusions can be drawn as to the effect which these various factors have in influencing co-ordination with different types of metal ions.

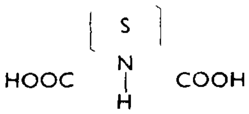
Because of the practical importance of the aminopolycarboxylic acids, an investigation of compounds related to the simplest aminopolycarboxylic acid, iminodiacetic acid (IMDA), would seem to be of interest. One compound of this type, dipicolinic acid, has been studied by GRENTHE(1), and the formation constants have been compared with those of IMDA.(2) Since the ring structure of piperidine-2,6-dicarboxylic acid might inhibit the movement of the carboxylate groups into a favourable co-ordination position, it was decided that this would be a logical ligand to investigate. Moreover, formation constant data are available for a number of other metal ions(3) and can be used for purposes of comparison.



IMDA



Dipicolinic Acid



Piperidine-2,6-dicarboxylic acid

EXPERIMENTAL

Preparation of piperidine-2,6-dicarboxylic acid. The piperidine-2,6-dicarboxylic acid was prepared by the hydrogenation of dipicolinic acid as described by ANDERSSON and SOINE.(4) The dipicolinic

(1) I. GRENTHE, *J. Amer. Chem. Soc.* **83**, 360 (1961).
(2) L. C. THOMPSON, *Inorg. Chem.* **1**, 490 (1962).
(3) R. M. TICHANE and W. E. BENNETT, *J. Amer. Chem. Soc.* **79**, 1293 (1957).
(4) N. E. ANDERSSON and T. O. SOINE, *J. Amer. Pharm. Assoc. (Sci. Ed.)* **39**, 460 (1950).

[illegible] Stone (Found C, 46 89, H [illegible] for C H O N ·H O [illegible] H [illegible] N 7 69%)

[illegible] solutions were prepared and standardized as [illegible] previously. The [illegible] solution was standardized potentiometrically [illegible] potassium hydroxide

[illegible] procedure consisted of potentiometric [illegible] the same equipment as described previously [illegible] potassium nitrate and the temperature was kept constant [illegible] was 0 0025 M and the ratio of ligand to rare earth ion was [illegible]

[illegible] pH [illegible] to concentration values using the correction factor [illegible] a dilute solution of nitric acid (μ 0 1 KNO₃) The con[illegible] determined using a value for K W of 1 68 10 [illegible] by the method outlined by CHABEREK and MARTELL[6] and the [illegible] both by solving simultaneous equations[7] and by the correction [illegible] method of IRVING and ROSSOTTI[8] The stability constants calculated by the two methods [illegible] 0 01 log K units

RESULTS AND DISCUSSION

The results which were obtained for the acid dissociation constants and the rare earth-piperidine-2,6-dicarboxylic acid formation constants are given in Table 1

TABLE 1 —FORMATION CONSTANTS FOR PIPERIDINE-2,6-DICARBOXYLIC ACID RARE EARTH CHELATES

	t 25°C		μ 0 10 (KNO₃)
	pK_1 2 54		pK_2 10 12
M³⁺	log K_1	log K_2	log β_2
La³⁺	5 31	4 06	9 37
Ce³⁺	5 69	4 50	10 19
Pr³⁺	5 83	4 78	10 61
Nd³⁺	5 92	4 88	10 80
Sm³⁺	6 13	5 30	11 43
Eu³⁺	6 13	5 32	11 45
Gd³⁺	6 09	5 37	11 46
Tb³⁺	6 16	5 43	11 59
Dy³⁺	6 26	5 56	11 82
Ho³⁺	6 32	5 55	11 87
Er³⁺	6 42	5 65	12 07
Tm³⁺	6 53	5 77	12 30
Yb³⁺	6 64	5 83	12 47
Lu³⁺	6 71	5 84	12 55
Y³⁺	6 00	5 40	11 40

The acid dissociation constants can be compared with the values of pK_1 = 2 87 and pK_2 = 9 92 (t 30°C, μ = 0 1 (KCl)) reported by Tichane and BENNETT[(3)]

---

* The rare earth oxides were generously supplied by Lindsay Chemical Division, American Potash and Chemical Corporation, West Chicago, Illinois

(5) L C THOMPSON, *J Inorg Nucl Chem* **24,** 1083 (1962),

(6) S CHABEREK, JR and A E MARTELL, *J Amer Chem Soc* **74,** 5052 (1952)

(7) B P BLOCK and G H MCINTYRE, JR , *J Amer Chem Soc* **75,** 5667 (1953)

(8) H IRVING and H S ROSSOTTI, *J Chem Soc* 3397 (1953)

Since the values of the 2:1 formation constants are rather small, the possibility of hydrolysis of the rare-earth ion must be considered. In order to minimize the hydrolysis, the experimental solutions contained a ligand to rare earth ratio of 5:1. This allows measurements to be made in a more basic range than is possible if a smaller is used. That hydrolysis does occur in the more basic regions is indicated by, the fact *that the calculated values of log K_2 show a strong upward trend.* Consequently the values which are reported were taken from the region preceding this upward trend. In general these formation constants were calculated from $\bar{n}$ values of 1.5 and less.

In order to check the experimental technique and computational procedure, the values of the formation constants for several metal ions with the ligand were determined using 5:1 solutions and these values were then compared with the literature values which were obtained using 2:1 solutions.(3) When allowance was made for the difference in temperature, the agreement was quite satisfactory (e.g. Co, log K_1 = 5.3 and log K_2 = 4.0, literature values, log K_1 = 5.4 and log K_2 = 4.1, Ni, log K_1 = 6.7 and log K_2 = 4.7, literature values, log K_1 = 6.8 and log K_2 = 4.8).

The log K_1 values show the usual trends which have been observed for rare-earth complexes of this type.(2) There is a uniform increase in the values as the atomic number increases with a slight decrease at gadolinium (the so-called "gadolinium break"). The value for yttrium, however, is much smaller than would have been predicted on the basis of its ionic size. Yttrium is consequently placed in the cerium earths between neodymium and samarium. It should also be noted that the overall spread in log K_1 values from lanthanum to lutetium is quite small, being only 1.4 log K units.

The trends in the log K_2 values are also the expected ones, with the exception of the small dip at holmium. The formation constant for the 2:1 yttrium complex has the more normal position between gadolinium and terbium. For each rare earth the value of log K_2 is larger than would be expected from the value of log K_1. The difference between the log K_1 and log K_2 values drops consistently in the cerium earths from 1.25 for lanthanum to 0.81 for europium, remains approximately constant at 0.75 through thulium, and then rises to 0.87 for lutetium. The somewhat different character of yttrium is shown by the fact that the corresponding difference is only 0.6. It is to be noted that all the rare earths heavier than samarium have values of log K_2 which are larger than K_1 for lanthanum. This behaviour has been observed previously only in the chelates of the rare earths with N,N′-ethylenediaminediacetic acid(5) and with 8-quinolinol-5-sulphonic acid,(9) but only in the former case was the effect so marked.

Since the skeletal chelating structures of the two ligands IMDA and piperidine-2,6-dicarboxylic acid are identical, it is of interest to compare them with respect to their chelation with the rare-earth ions. Of particular concern are the differences in the corresponding log K_1 and log K_2 values. These differences are given in Table 2.

The 1:1 IMDA chelates are more stable than the corresponding piperidine-2,6-dicarboxylic acid chelates. Since the latter molecules is somewhat strained when it is co-ordinated, as indicated by molecular models,(3) it would be expected to form complexes which are less stable than IMDA even though the nitrogen atom is more basic. The fact that the difference in the log K_1 values is

---

(9) B. F. Freasier, A. G. Oberg and W. W. Wendlandt, *J. Phys. Chem.* **62**, 700 (1958).

TABLE 2.—DIFFERENCES BETWEEN THE FORMATION CONSTANTS OF THE RARE EARTH-IMDA AND -PIPERIDINE-2,6-DICARBOXYLIC ACID CHELATES (Pip)

M^{3+}	$\log K_1$ LnIMDA − $\log K_1$ LnPip	$\log K_2$ LnIMDA − $\log K_2$ LnPip
La^{3+}	0.57	0.03
Ce^{3+}	0.49	0.03
Pr^{3+}	0.61	0.00
Nd^{3+}	0.58	0.01
Sm	0.51	0.06
Eu^{3+}	0.60	0.06
Gd^{3+}	0.60	0.02
Tb^{3+}	0.62	0.03
Dy^{3+}	0.62	0.13
Ho^{3+}	0.64	0.05
Er^{3+}	0.67	0.06
Tm^{3+}	0.69	0.09
Yb^{3+}	0.78	0.02
Lu^{3+}	0.90	0.28
Y^{3+}	0.78	0.15

approximately constant through dysprosium and then increases to lutetium might be an indication that the larger rare-earth ions are better able to overcome the adverse steric effect imposed by the piperidine ring on the ease with which the carboxylate groups can approach the metal ion. A similar type of effect was noted with the dipicolinic acid complexes.(2,10)

The 2:1 IMDA chelates and the 2:1 piperidine-2,6-dicarboxylic acid chelates are of nearly the same stability. In view of the differences in stabilities of the 1:1 chelates, this is somewhat unexpected. A possible explanation for this is contained in the steric factor mentioned in connection with the 1:1 chelates.

In order to provide some other evidence for this steric effect the formation constants of the piperidine-2,6-discarboxylic acid chelates of cadmium were determined. (Cadmium was selected since it forms complexes with aminopolycarboxylic acids which have formation constants of the same magnitude as the rare earths and its IMDA and dipicolinic acid chelates exhibit the same trends as the corresponding rare-earth complexes.(2,10) This is probably due to the fact that it has an ionic radius which falls in the range of the ionic radii of the rare earths.) A comparison of the formation constants which were obtained ($\log K_1 = 5.22$ and $\log K_2 = 4.42$, $t = 25°C$) with the corresponding IMDA values ($\log K_1 = 5.35$ and $\log K_2 = 4.18$, $t = 30°C$) reveals that the cadmium chelates with this ligand are also influenced in much the same way as the rare-earth chelates.

It would appear that in the 2:1 piperidine-2,6-dicarboxylic acid chelates of ions having rather larger ionic radii, such as cadmium and rare earths, the adverse effect of the strain in the piperidine ring is partially smoothed out and the increased basicity of the nitrogen atom becomes the more important factor.

Acknowledgement—This work was supported by a PHS research grant GM 08394-02 from the Division of General Medical Studies, Public Health Service. The assistance of Miss J. A. LORAAS with some of the experimental measurements is gratefully acknowledged.

---

(10) G. ANDEREGG, *Helv. Chim. Acta* **43**, 414 (1960).

J. Inorg. Nucl. Chem. 1963, Vol. 25, pp. 823 to 827. Pergamon Press Ltd. Printed in Northern Ireland

IRON(III) DIMETHOXIDE COMPOUNDS

K. STARKE
Institut für Kernchemie, Universität Marburg, Marburg (Lahn), Germany

(*Received* 15 *November* 1962, *in revised form* 18 *January* 1963)

Abstract—The preparation of various anhydrous iron(III) compounds and their conversion to iron(III) dimethoxides of the type $Fe(OCH_3)_2X$ are described. The formate and the acetate were synthesized by improved, convenient methods and new alkanoates (stearate, pivalate, benzoate, adipate, chloroacetate and trichloroacetate) were obtained. Also, the nitrate and compounds with the anions of ethyl acetoacetate, dibenzoylmethane and thenoyltrifluoroacetone were made. Attempts to prepare derivatives of strong acids and complexing agents are briefly discussed.

HOFMANN and BUGGE$^{(1)}$ allowed iron to react with formic and acetic acids in methanol and, by oxidation, obtained precipitates of the composition $Fe(OCH_3)_2OCOR$ ($R = H, CH_3$).

$$4Fe(OCOR)_2 + 8CH_3OH + O_2 \rightarrow 4Fe(OCH_3)_2OCOR + 4HOCOR + 2H_2O \quad (1)$$

The striking, canary yellow products also attracted the attention of WEINLAND and HOLTMEIER$^{(2)}$ who treated the dark red basic acetates with excess methanol.

$$Fe_3(OH)_2(OCOCH_3)_7 + 6CH_3OH \rightarrow 3Fe(OCH_3)_2OCOCH_3 + 4HOCOCH_3 + 2H_2O \quad (2)$$

Recently, HARDT and MÖLLER$^{(3)}$ reported properties of iron(III) dimethoxide acetate obtained by reaction (1). The compound was also encountered during an investigation of basic iron(III) acetates.$^{(4)}$ It seemed worthwhile to study the preparation of iron(III) methoxide compounds because of the apparent ease of formation and their relative stability.

Methanolysis of an iron(III) compound is the essential step in the formation of methoxide compounds.

$$FeX_3 + 2CH_3OH \rightleftharpoons Fe(OCH_3)_2X + 2HX \quad (3)$$

Completing the reaction is mainly a question of removing the acid HX from the equilibrium. The by-products must be prevented from contaminating the precipitates, which cannot be recrystallized. Starting from iron or iron(II) is neither necessary nor desirable, because water is introduced by the subsequent oxidation. Though traces can be tolerated, the main problem is finding anhydrous iron(III) compounds suitable as starting materials.

Iron(III) nitrate 9-hydrate was used in some preparations as the nitrate ion is replaced most easily and can be removed by reduction. Also, many nitrates are reasonably soluble in methanol. The water of hydration was either evaporated during the preparation or was allowed to react with 2,2-dimethoxypropane to yield methanol and acetone.(5) It can also be substituted by dimethylsulphoxide,(6,7) which then, in addition to methanol, serves as solvent for the by-products. Anhydrous iron(III) chloride was used for the preparation of iron(III) ethyl acetoacetate. With some alkanoic acids it allows a most simple synthesis, ethyl acetoacetate being the only by-product.

---

(1) K. A. HOFMANN and G. BUGGE, *Ber. Dtsch. Chem. Ges.* **40**, 3764 (1907).
(2) R. WEINLAND and H. HOLTMEIER, *Z. Anorg. Chem.* **173**, 49 (1928).
(3) H. D. HARDT and W. MÖLLER, *Z. Anorg. Chem.* **313**, 57 (1961).
(4) K. STARKE, *J. Inorg. Nucl. Chem.* **13**, 254 (1960).

$$\mathrm{Fe(CH_3COCHCOOC_2H_5)_3 + HOCOR + 2CH_3OH} \rightarrow \mathrm{Fe(OCH_3)_2OCOR + 3CH_3COCH_2COOC_2H_5} \quad (4)$$

EXPERIMENTAL

Materials

Unless stated otherwise the chemicals were of analytical reagent purity. The solvents were of practical grade. The ligroine had a boiling range of 30–50 C. Volume ratios are given for solvent mixtures.

Analysis

All data are averages of two determinations. The samples were dissolved in standard sulphuric acid. Iron(III) was determined iodometrically. The iron(II) was then precipitated as hexacyanocobaltate(III), iodate was added and the acid determined iodometrically.(8) The molar ratio of basic groups, (OH, OCH_3):Fe was calculated from the amount of acid neutralized by the sample. Because the method fails with very weak acids or strong complexing agents, this ratio cannot be reported for all compounds. Microanalyses were carried out by the Microanalytical Laboratory, Max-Planck-Institut fur Kohlenforschung, Mulheim (Ruhr), Germany.

Preparations

All products were dried and kept in a vacuum desiccator over silica gel. In view of the debatable molecular weights of some basic iron compounds yields are sometimes expressed in percentage of iron recovered.

1. Starting materials. (a) Iron(III) nitrate 9-hydrate (8.08 g, 0.02 mole) was allowed to react with formic acid (7.36 g, 0.16 mole), the nitrate being reduced to nitrous oxides. The mixture was evaporated to dryness on the water bath, the residue taken up with methanol-formic acid (1:1) *and dried carefully to avoid overheating. There remained 3.81 g (96.6 per cent of iron).* (Found: Fe, 28.31%, OH:Fe, 0.8.) The product was dissolved in 2 ml of formic acid and reprecipitated with excess 2,2-dimethoxypropane. The amount obtained was 0.93 g (97.5 per cent of iron). (Found: Fe, 29.67%, OH:Fe, 0.5.) Commercial iron(III) formate was also used. (Found: Fe, 26.86%, OH:Fe 0.8. Calc. for $Fe(OCOH)_3$: Fe, 29.25%, OH:Fe, 0.0.)

(b) Iron(III) nitrate 9-hydrate (40.4 g, 0.10 mole) and trichloroacetic acid (53.9 g, 0.33 mole) were dissolved in 100 ml of 2-propanol, which acted as reducing agent for the nitrate. The solution was warmed on the water bath in small portions to avoid a too vigorous liberation of nitrous oxides. After evaporation to dryness the residue was dried in the oven at 60 C. There remained 44.0 g (94.9 per cent of iron). (Found: Fe, 12.05%, OH:Fe, 0.5.) The product (3.00 g) was warmed with 3.00 g of trichloroacetic acid in 3.0 ml of toluene. The precipitate was washed with benzene. The amount obtained was 2.75 g (89.3 per cent of iron). (Found: Fe, 11.74%, OH:Fe, 0.4. Calc. for $Fe(OCOCCl_3)_3$: Fe, 10.29%, OH:Fe, 0.0.)

(c) Iron(III) nitrate 9-hydrate (8.08 g, 0.02 mole) in 10 ml of acetone was mixed with dimethylsulphoxide (11.0 g) and more acetone was added. It was also used to wash the crystals, which were separated by suction. The amount obtained was 13.5 g (94.2 per cent of theory). (Found: Fe, 8.16%, OH:Fe, 0.0.) The residues of three preparations were concentrated. Large greenish crystals were formed after several days. (Found: Fe, 8.05, C, 20.66, H, 5.09, N, 5.70, S, 26.75. Calc. for $Fe[(CH_3)_2SO]_6(NO_3)_3$: Fe, 7.86, C, 20.28, H, 5.11, N, 5.91, S, 27.07%, OH:Fe, 0.0.)

---

(5) K. STARKE, *J. Inorg. Nucl. Chem.* **11,** 77 (1959).

(6) H. L. SCHLAFER and W. SCHAFFERNICHT, *Angew. Chem.* **72,** 618 (1960).

(7) F. A. COTTON and R. FRANCIS, *J. Amer. Chem. Soc.* **82,** 2986 (1960); *J. Inorg. Nucl. Chem.* **17,** 62 (1961).

(8) K. STARKE, *Analyt. Chem.* In press.

(d) Iron(III) chloride (sublimed, practical grade, 16 2 g, 0 10 mole) and ethyl acetoacetate (39 0 0 30 mole) were dissolved in 200 ml of ether Dry ammonia gas was passed through until ammon- n chloride was completely precipitated It was separated by suction and the ether pumped off in a uum while the filtrate was introduced in small portions and cooled with ice There remained 37 9 g 5 per cent of theory) (Found Fe, 12 82%) Part of the product was recrystallized by treating e ether solution with charcoal and pumping off the ether in the manner described (Found C, 61 H 6 09 Calc for $Fe(CH_3COCHCOOC_2H_5)_3$ Fe, 12 60, 48 78, H, 6 14%) The m p was 0 C, which was also found for a sample prepared with sodium ethyl acetoacetate according to KNORR nd SCHUBERT[9] This is not in agreement with the m p of 99 100 C reported by these authors

2 Iron(III) dimethoxide compounds The crude products 1 a d were used in the following eparations (a) Iron(III) formate (practical grade 3 00 g) was heated with 400 ml of methanol ntil the red starting material had disappeared The yellow precipitate was separated by suction nd washed with methanol The amount obtained was 1 46 g (60 8 per cent of iron) (Found Fe, 33 54, OCH_3 Fe, 2 00) Iron(III) formate (prepared by procedure 1a, 2 00 g) was treated the ame way The amount obtained was 0 6 g (37 1 per cent of iron) (Found Fe, 34 98%, OCH_3 Fe, 2 00 Calc for $Fe(OCH_3)_2OCOH$ Fe, 34 28%, OCH_3 Fe, 2 0)

(b) Iron(III) trichloroacetate (prepared by procedure 1b, 3 00 g) was dissolved in 400 ml of methanol A precipitate was formed, which increased on warming and was allowed to settle It was washed with methanol and separated by suction The amount obtained was 1 70 g (92 1 per cent of iron) (Found Fe, 19 59%, OCH_3 Fe, 1 8) Iron(III) nitrate 9-hydrate (2 02 g, 0 005 mole) was allowed to react with 50 ml of 2,2-dimethoxypropane Trichloroacetic acid (0 82 g, 0 005 mole) was added The precipitate was allowed to settle, separated by suction and washed with 2,2-dimethoxypropane The amount obtained was 1 31 g (93 5 per cent of theory) (Found Fe, 20 07, C, 16 89, H, 2 05%, OCH_3 Fe, 2 0) Calc for $Fe(OCH_3)_2OCOCCl_3$ Fe, 19 92 C, 17 14, H, 2 16%, OCH_3 Fe, 2 0)

(c) Iron(III) nitrate 9-hydrate (4 04 g, 0 01 mole) was allowed to react with 100 ml of 2,2-dimethoxypropane The solution was diluted with 400 ml of benzene-ligroine (1 1) and left for several days The greenish-yellow crystals were separated by suction and washed with 2,2-dimethoxypropane in a dry box The amount obtained was 1 73 g (96 2 per cent of theory) The compound decomposed, the carbon and nitrogen contents decreasing in successive determinations (Found in the first determination Fe, 30 90, C, 11 96, 3 19, N, 7 00%, OCH_3 Fe, 1 9) The compound was also prepared with toluene-ligroine (1 1) as precipitating agents The amount obtained was 1 68 g (93 4 per cent of theory) The nitrate was precipitated with nitron (Found Fe, 30 94, NO_3, 33 25%, OCH_3 Fe, 1 9 Calc for $Fe(OCH_3)_2NO_3$ Fe, 31 04, C, 13 35, H, 3 36, N, 7 79, NO_3, 34 46%, OCH_3 Fe, 2 0)

(d) Hexakis(dimethylsulphoxide) iron(III) nitrate (3 55 g, 0 005 mole) and sodium acetate (2 46 g, 0 03 mole), each dissolved in 40 ml of methanol, were mixed and warmed on the water-bath The precipitate was separated by centrifugation and washed with methanol The mother liquor combined with the washings yielded an additional quantity The total amount obtained was 0 60 g (67 8 per cent of theory) (Found Fe, 31 24%, OCH_3 Fe, 2 0) Iron(III) ethyl acetoacetate (2 22 g 0 005 mole) and ammonium acetate (2 31 g, 0 03 mole), each dissolved in 40 ml of methanol, were treated in the manner described The amount obtained was 0 76 g (85 9 per cent of theory) (Found Fe, 31 50%, OCH_3 Fe, 2 0 Calc for $Fe(OCH_3)_2OCOCH_3$ Fe, 31 56%, OCH_3 Fe, 2 0)

(e) Iron(III) ethyl acetoacetate (4 43 g, 0 01 mole) and chloroacetic acid (0 95 g 0 01 mole), each dissolved in 75 ml of methanol, were mixed and treated in the manner described (2d) The amount obtained was 1 82 g (86 1 per cent of theory) (Found Fe, 26 49%, OCH_3 Fe, 2 1 Calc for $Fe(OCH_3)_2OCOCH_2Cl$ Fe, 26 42%, OCH_3 Fe, 2 0)

(f) Same procedure with pivalic acid (1 02 g, 0 01 mole) The amount obtained was 2 06 g (94 0 per cent of theory) (Found Fe, 25 13%, OCH_3 Fe, 2 1 Calc for $Fe(OCH_3)_2OCOC(CH_3)_3$ Fe, 25 50%, OCH_3 Fe, 2 0)

(g) Same procedure with stearic acid (2 85 g, 0 01 mole) The amount obtained was 2 26 g (58 5 per cent of theory) (Found Fe, 14 89% Calc for $Fe(OCH_3)_2OCO(CH_2)_{16}CH_3$ Fe, 14 46%)

(h) Same procedure with adipic acid (0 73 g, 0 005 mole) The amount obtained was 1 83 g (96 3 per cent of theory) (Found Fe, 28 66%, OCH_3 Fe, 2 0 Calc for $Fe(OCH_3)_2OCO(CH_2)_4COOFe(OCH_3)_2$ Fe, 29 40%, OCH_3 Fe, 2 0)

(9) L KNORR and H SCHUBERT, *Ber Dtsch Chem Ges* **44,** 2772 (1911)

(j) Same procedure with benzoic acid (1 22 g 0 01 mole) The amount obtained was 2 10 g (*87 9 per cent of theory*) (*Found Fe 23 36 %, OCH_3 Fe, 2 2 Calc for* $Fe(OCH_3)_2OCOC_6H_5$ *Fe 23 36 %, OCH_3 Fe, 2 0*)

(k) *Iron(III) ethyl acetoacetate (4 43 g, 0 01 mole)* was dissolved in 300 ml of methanol After 4 days the orange precipitate was separated by suction and washed with methanol and 2,2-dimethoxypropane The amount obtained was 1 60 g (64 8 per cent of theory) (Found Fe, 23 18, C 38 11 H, 5 94 Calc for $Fe(OCH_3)_2CH_3COCHCOOC_2H_5$ Fe, 22 61, C, 38 89, H, 6 12 %) The starting material yielded the same compound in attempts to prepare iron(III) dimethoxide perchlorate and trifluoroacetate

(l) Hexakis(dimethylsulphoxide) iron(III) nitrate (7 11 g, 0 01 mole) and dibenzoylmethane (2 24 g, 0 01 mole) were dissolved in 100 ml of methanol A solution of dry ammonia gas in methanol was added until precipitation was complete The orange precipitate was separated by centrifugation and washed with methanol The amount obtained was 3 10 g (90 9 per cent of theory) (Found Fe, 17 09 C, 58 09 H, 4 72 Calc for $Fe(OCH_3)_2C_6H_5COCHCOC_6H_5$ Fe, 16 37, C, 59 85, H, 5 02 %)

(m) Same procedure with thenoyltrifluoroacetone (2 22 g, 0 01 mole) A yellow precipitate was separated The amount obtained was 2 95 g (87 0 per cent of theory) (Found Fe, 15 61, C, 34 82, H, 2 97 S, 9 38 Calc for $Fe(OCH_3)_2CF_3COCHCOC_4H_3S$ Fe, 16 47, C, 35 42, H, 2 97, S, 9 46 %)

RESULTS AND DISCUSSION

Though for a long time sole representatives of iron(III) methoxide compounds, the formate and acetate are not unique This is demonstrated by the preparation of precipitates with various other anions While HOFMANN and BUGGE(1) regarded their compounds as dimethoxides, HARDT and MOLLER(3) reported for the acetate a variable composition, $[Fe(OCH_3)_{2\ x}(OCOCH_3)_{1\ x}]_n$ (1   x - 0)

In the present investigation, the average of the ratios OCH_3 Fe that were determined is close to two, with deviations to both sides of up to 10 per cent This is greater than the analytical error Complicated formulas different from that of a dimethoxide might be advanced for some precipitates However, there is doubt that such formulas represent definite compounds unless the same composition is obtained under varied conditions The objective of the present investigation was to prepare many different compounds A couple of them were made in two ways, the ratios being 1 8, 2 0 (trichloroacetate) and 2 0, 2 0 (acetate) Pending the results of further studies, the compounds are best described as polynuclear complexes of a general formula, $[Fe(OCH_3)_{2\ m}X_{1\ m}]_n$ (0 2 m 0 2) The nomenclature for basic salts was used

The difficulties of isolating compounds with constant composition remind of the aqueous system There, the analogous condensation by olation may be followed by the process of oxolation Unlike hydroxide, the methoxide group has no hydrogen or other ion to lose This could partly explain the relatively small range in composition of methoxide compounds in contrast to basic acetates which extend from complexes like $Fe_3(OH)_2(OCOCH_3)_6^{+}$ to polymeric products such as $[Fe_3O_3(OH)_2OCOCH_3]_n$

The solvated iron(III) probably loses protons easily, methanol resembling water more than any of the higher alcohols With ammonia as acceptor, BRADLEY, MULTANI and WARDLAW(10) removed three protons per iron atom by precipitation as ammonium chloride and obtained iron trimethoxide

$$3FeCl_3(CH_3OH)_3 + 9NH_3 \rightarrow Fe_3(OCH_3)_9 + 9NH_4Cl \downarrow \qquad (5)$$

A trimer with methoxide bridges, the compound is soluble in methanol and benzene

---

(10) D C BRADLEY, R K MULTANI, W WARDLAW, *J Chem Soc* 126 (1958).

Attempts to prepare an iron methoxide chloride according to preparation 2c failed, while the nitrate separated only slowly after addition of a benzene-ligroine mixture Methoxide compounds of perchloric, sulphuric and trifluoroacetic acids could not be observed They may be too soluble to be isolated without using long lasting procedures requiring careful exclusion of moisture

The iron methoxide compounds described in the present paper are relatively insoluble in methanol and could therefore be separated rapidly Possibly, the respective acid anions act as bridges in the formation of polynuclear complexes This would also explain why the anions of strong acids such as perchlorate, sulphate and trifluoroacetate, which are weak donors, do not cause precipitation Only after trichloroacetic acid (preparation 2b) and other alkanoic acids are added to a nitrate solution does an alkanoate separate Ethyl acetoacetate of the starting material is incorporated in the precipitate rather than perchlorate or trifluoroacetate ions added (preparation 2k)

While methoxide groups replace two of three ethyl acetoacetate groups (preparation 2k), they fail to do so with other, evidently stronger complexing agents For instance, iron methoxide compounds of oxalic and salicylic acids could not be obtained, colour changes indicating that the normal chelates of these acids were formed

Further research must concentrate on preparation of pure representatives of the series and X-ray analysis of their crystal structure This could settle the question whether the composition is variable or exactly that of a dimethoxide

Acknowledgements—The financial support by the Bundesministerium fur Atomkernenergie and the Fonds der Chemischen Industrie is gratefully acknowledged Thanks are also due to the Dow Chemical Company, Midland, Michigan, for a generous supply of 2 2-dimethoxypropane

J Inorg Nucl Chem 1963, Vol 25, pp 829 to 831 Pergamon Press Ltd Printed in Northern Ireland

PHOSPHORUS THIOBROMIDES

J M ANDREWS, J E FERGUSSON and C J WILKINS
Department of Chemistry, University of Canterbury, Christchurch, New Zealand

(*Received* 28 *December* 1962, *in revised form* 15 *February* 1963)

Abstract—Besides thiophosphoryl tribromide there exist two crystalline thiobromides, $P_2S_6Br_2$ and $P_2S_5Br_4$, both of which are obtained from the bromination of tetraphosphorus heptasulphide

THE compositions of the phosphorus thiohalides are dependent upon the halogen Thiophosphoryl trihalides, PSX_3, are known where X = F, Cl, and Br, but the only thiodide is $P_4S_3I_2$(1) related structurally to the phosphorus sulphides(2) Other thiobromides $P_2S_3Br_4$, P_2SBr, and P_2SBr_6 were reported in 1872 by MICHAELIS(3) but without adequate evidence of their identity as pure compounds The first two were said to be obtained by the bromination of "P_2S_3" and the last from the decomposition of thiophosphoryl tribromide under distillation Re-examination of the bromination products shows them to comprise phosphorus tribromide, thiophosphoryl tribromide and two new crystalline sulphur-rich thiobromides, diphosphorushexathiodibromide, $P_2S_6Br_2$, and diphosphoruspentathiotetrabromide, $P_2S_5Br_4$ The first with its higher proportion of sulphur is obtained in higher yield from pure tetraphosphorus heptasulphide than from "P_2S_3" which contains both the heptasulphide and lower sulphides in admixture (4)

An examination of other reactions, which on the basis of early claims, might yield other thiobromides failed to reveal such products Distillation of thiophosphoryl tribromide at atmospheric pressure causes dissociation to phosphorus tribromide and sulphur Cryoscopic measurement of molecular weights of mixtures of phosphorus tribromide or tetraphosphorus decasulphide with thiophosphoryl tribromide gave no evidence of association or rearrangement

Of the phosphorus sulphides the decasulphide alone fails to react with bromine This suggests that initial attack occurs at the P—P bonds present in all but the decasulphide Tetraphosphorus trisulphide yields the heptasulphide as an intermediate product, which is indicative of considerable atomic rearrangement during the reaction Some interconversion of molecular species must continue even after the bromination because in the isolation of the thiobromides the two compounds crystallize from the solvent *in succession*

The two thiobromides can be recovered unchanged from carbon disulphide and molecular weights were determined ebullioscopically in this solvent In polar solvents, however, decomposition occurs Contact with acetonitrile at ordinary temperatures causes conversion to thiophosphoryl tribromide and an insoluble residue, one constituent of which is low in bromine, but no known phosphorus sulphides are present

---

(1) R D TOPSOM and C J WILKINS, *J Inorg Nucl Chem* **3**, 187 (1956)

(2) D A WRIGHT and B R PENFOLD, *Acta Cryst* **12**, 455 (1959)

(3) A MICHAELIS, *Liebigs Ann* **164**, 9 (1872)

(4) G A RODLEY and C J WILKINS, *J Inorg Nucl Chem* **13**, 231 (1960)

Phosphoryl tribromide and this same product of low bromine content are also formed (along with phosphorus tribromide) from thermal decomposition of the thiobromides in the absence of solvent

The infra-red spectra of the crystalline compounds (Fig 1) have the features associated with the P=S and P—S—P linkages of the phosphorus sulphides [5] The strong absorption within the range 650–680 cm^{-1} characteristic of the three sulphides having P=S bonds (spectra *b*, *c* and *d*) is shown also by the two thiobromides (*e* and *f*), and both show bands at 450–520 cm^{-1} due to the P—S—P group The spectrum of diphosphorushexathiodibromide resembles that of tetraphosphorus decasulphide most closely, but in common with the *lower* phosphorus sulphides the spectra of both thiobromides also show absorptions at 400–450 cm^{-1} Assuming that the coordination number of phosphorus towards sulphur is limited to four the compositions of the thiobromides require that S—S bonds must also be present Absorptions due to such bonds may appear within the same region[6], but these are weak in other classes of compounds The densities of the thiobromides ($P_2S_6Br_2$, 1 82, $P_2S_5Br_4$, 1 99 g cm^{-3}) are low, falling even below the range 2 03–2 19 for the phosphorus sulphides This evidence of an unusually open packing renders any ionic structure improbable An X-ray determination of the crystal structure of diphosphorushexathiodibromide is being made in this laboratory by Dr B R PENFOLD

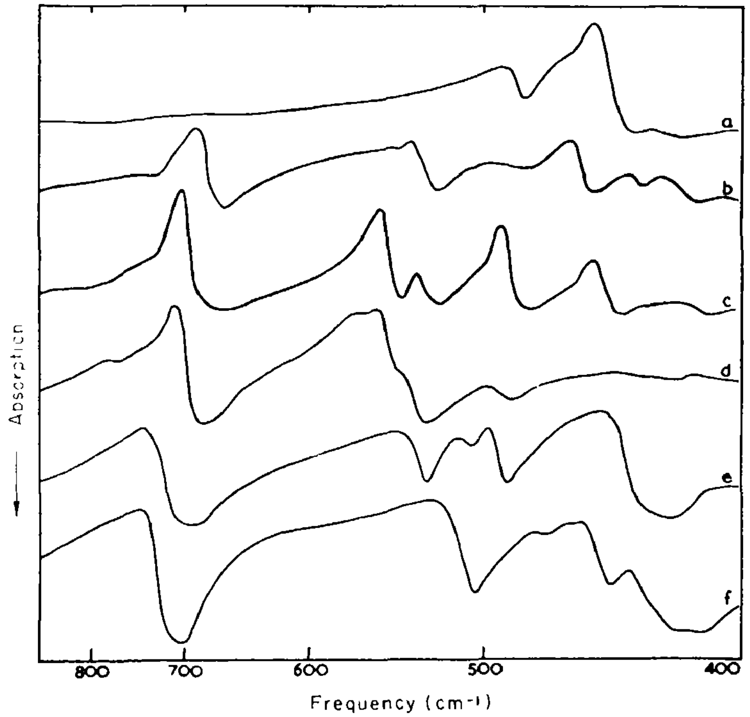


FIG 1 – Infra-red spectra of (a) P_4S_3, (b) P_4S_5, (c) P_4S_7, (d) P_4S_{10}, (e) $P_2S_6Br_2$, (f) $P_2S_5Br_4$

---

[5] See also A PITOCHELLI and L F AUDRIETH, *J Amer Chem Soc*, **81**, 4458 (1959)

[6] L J BELLAMY, *The Infra-red Spectra of Complex Molecules* (2nd Ed), p 352 Methuen, London (1958)

EXPERIMENTAL

Preparation and properties of the thiobromides Dry bromine (72 g) was added to an ice-cold suspension of sieved (40 mesh) tetraphosphorus heptasulphide (50 g) in pure carbon disulphide An hour was allowed for the addition and stirring continued for a further 30 min before the solution was siphoned from any unreacted sulphide Solvent was distilled off until the temperature of the remaining oil had risen to 80° Ether was added until the precipitate which formed initially just redissolved and the solution shaken vigorously to dissolve as much of the oil as possible Needle-like crystals of the diphosphorushexathiodibromide (3 g) appeared within an hour, to be followed by much slower crystallization of nodules of diphosphoruspentathiotetrabromide (4 g) The residual oil solidified to a mixture of the two compounds as shown by X-ray powder photography Throughout the preparations solutions were kept under carbon dioxide and the crystalline compounds handled in a dry box The same reaction products were obtained even when heating was avoided by removing solvent under vacuum

Analyses were carried out as for the thiodide[1] (Found, diphosphorushexathiodibromide P, 14 82, 14 85, S, 45 36, 45 38, Br, 38 49, 38 66%, *m*, 360 Calc for $P_2S_6Br_2$ P, 14 98, S 46 40, Br, 38 62%, *m*, 414 Found, diphosphoruspentathiotetrabromide, P, 11 61, 11 69, S, 29 53, 29 29, 29 70, Br, 57 73, 57 63, and 58 4 on a different sample, *m*, 583 Calc for $P_2S_5Br_4$ P, 11 44, S, 29 58, Br, 58 98% *m*, 542) The hexathiodibromide melts at 118°, and the pentathiotetrabromide at 90°, both with decomposition

Decomposition of diphosphoruspentathiotetrabromide (5 56 g) heated to 200° under high vacuum gave phosphorus tribromide (1 13 g) and thiophosphoryltribromide (1 70 g) The solidified residue (21 5% Br) gave X-ray powder lines with *d*, 6 07 *m* and 3 16 *s* The residue from the pentathiotetrabromide in acetonitrile gave these and additional lines having *d* values 4 61 *m*, 3 78 *w*, 3 69 *w*, 3 52 *w*, 3 42 *w*, 3 32 *w*, 2 63 *w*, 2 57 *w*, 2 19 *w* The original thiobromides give *d* values $P_2S_6Br_2$, 5 75 *w*, 4 47 *s*, 3 45 *m*, 2 97 *s*, 2 41 *m*, 2 27 *m*, 1 72 *w*, 1 66 *w*, 1 60 *w*, and for $P_2S_5Br_4$, 5 09 *s*, 4 73 *s*, 3 98 *m*, 3 43 *w*, 3 18 *m*, 3 04 *m*, 3 00 *m*, 2 97 *m*, 2 70 *m*, 2 26 *w*, 2 00 *w*, 1 83 *w*

Densities were measured by flotation in mixtures of carbon tetrachloride and ethylene dibromide Infra-red spectra were run on Nujol mulls using a Perkin Elmer 221 spectrophotometer with potassium bromide optics

Acknowledgements—The authors are indebted to Messrs C G FREEMAN and R. E J HUTCHINSON and Miss P S MARKHAM, for assistance with experimental work

J Inorg Nucl Chem 1963, Vol 25, pp 833 to 842 Pergamon Press Ltd Printed in Northern Ireland

THE THERMAL DECOMPOSITION OF METAL COMPLEXES—IV

SOME AMINE COMPLEXES OF COPPER (II) SULPHATE

W W Wendlandt
AFOSR Centre for Molecular Research, Department of Chemistry,
Texas Technological College, Lubbock, Texas

(*Received* 8 *October* 1962, *in revised form* 27 *December* 1962)

Abstract—The thermal dissociation of the *mono-*, *bis-*, and *tris*-(ethylenediamine)–, the *bis*(1,2-propanediamine)–, and the *bis*(1,3-propanediamine)–complexes of copper (II) sulphate was studied by thermogravimetry, differential thermal analysis, gas evolution, and high temperature reflectance spectroscopy The TGA curve obtained for $[Cu(en)_3]SO_4$ corresponded to that expected for the deamination of one of the ethylenediamines The decomposition curves of the *bis*(amine)–complexes corresponded to a one step deamination process, giving $CuSO_4$ which immediately dissociated into CuO and SO_3 The E_a for the deaquation of $[Cu(en)(H_2O)_2]SO_4$ was 29 kcal $mole^{-1}$ as determined by a DTA method Reflectance curves are given for all of the complexes at ambient temperature as well as $[Cu(en)(H_2O)_2]SO_4$ at elevated temperatures

The ethylenediamine (en) complexes of the copper (II) salts are well known Previous studies have been concerned with their preparation and properties,(1–8) thermochemistry,(9–11) structure,(12–15) absorption spectra and composition,(16) and optical rotation (5) Perhaps the least studied property of these complexes has been their thermal stability although the drying and dehydration temperatures have been recorded for some of them (4,5) It is thus the object of this investigation to study the thermal properties of the *mono-*, *bis-*, and *tris*(ethylenediamine)- the *bis*(1,2-propanediamine)- and the *bis*(1,3-propanediamine)-complexes of copper (II) sulphate

EXPERIMENTAL

Reagents The ethylenediamine and 1,2-propanediamine (pn) were obtained from Eastman Organic Chemicals, Rochester, N Y The 1,3-propanediamine (trimethylenediamine, tm) was obtained from

---

(1) P Pfeiffer and S V Mullenhein, *J Prakt Chem* **137,** 9 (1933)
(2) F W Chattaway and H D K Drew, *J Chem Soc* 947 (1937)
(3) P Pfeiffer and H Glaser, *J Prakt Chem* **151,** 134 (1938)
(4) C M. Harris, *J Proc Roy Soc N S Wales* **82,** 218 (1948), **85,** 138 (1952)
(5) G Gordon and R K Birdwhistell *J Amer Chem Soc* **81,** 3567 (1959)
(6) W Wahl, *Soc Sci Fennica Commentationes Phys Math* **4,** [14] 1 (1927), *Chem Abstr* **22,** 3596 (1928)
(7) J J Fritz, R Rao and S Seki, *J Phys Chem* **62,** 703 (1958)
(8) C H Johnson and S A Bryant, *J Chem Soc* 1338 (1945)
(9) C G Spike and R W Parry, *J Amer Chem Soc* **75,** 3770 (1953)
(10) T Davies, S S Singer and L A K Staveley *J Chem Soc* 2304 (1954)
(11) I Poulsen and J Bjerrum, *Acta Chem Scand* **9,** 1407 (1955)
(12) K S Mandal, *Current Sci* **10,** 78 (1941)
(13) H Scouloudi and C H Carlisle, *Nature* **166,** 357 (1950)
(14) H Scouloudi, *Acta Cryst* **6,** 651 (1953)
(15) G Giuseppetti and F Mazzi, *Rend Soc Mineralog Ital* **11** 202 (1955)
(16) H B Jonassen and T H Dexter *J Amer Chem Soc* **71,** 1553 (1949)

the American Cyanamid Co , New York, N Y They were all purified by conventional methods Reagent grade copper (II) sulfate 5-hydrate was obtained from the Mallinckrodt Chemical Works, St Louis, Mo

Preparation of complexes The compounds, $[Cu(en)(H_2O)_2]SO_4$, $[Cu(en)_2]SO_4$ and $[Cu(en)_3]SO_4$, were prepared as previously described [illegible] The $[Cu(pn)_2]SO_4$ and $[Cu(tm)_2]SO_4$ were prepared by the same procedure as was used for $[Cu(en)_2]SO_4$

The compounds were analysed for copper content by ignition to CuO in a muffle furnace at 850 C The carbon and hydrogen analyses were determined by the Schwarzkopf Microanalytical Lab , Woodside 77, N Y The results of the analyses are given in Table I

TABLE 1 – ANALYSES OF COPPER COMPLEXES

Compound	% Copper		% Carbon		% Hydrogen	
	Found	Theor	Found	Theor	Found	Theor
$[Cu(en)(H_2O)_2]SO_4$	25 24	24 84	9 80	9 39	4 58	4 73
$[Cu(en)_2]SO_4$	22 62	22 71	17 23	17 17	5 98	5 76
$[Cu(en)_3]SO_4$	18 80	18 69	21 33	21 20	7 23	7 12
$[Cu(pn)_2]SO_4$	19 88	20 64	22 12	23 41	7 00	6 55
$[Cu(tm)_2]SO_4$	20 90	20 64	21 98	23 41	6 88	6 55

Thermobalance The automatic recording thermobalance has previously been described [17] Sample sizes range in weight from 50–55 mg The furnace heating rate was approximately linear with time at 7°C per min An air atmosphere was maintained in the furnace during the pyrolysis process

Differential thermal analysis apparatus The differential thermal analysis apparatus has been previously described [18] Sample sizes ranged in weight from 40 to 50 mg and were pyrolysed under a dynamic helium atmosphere at a furnace heating rate of 10 ± 1 C per min The gas evolution curves were recorded either on a Varian Model G-22 strip chart recorder or a Moseley Model 135R X Y recorder

Reflectance spectra studies The reflectance curves were obtained using a heated sample holder[19] attached to the reflectance unit of a Bausch and Lomb Spectronic 505 spectrophotometer The reflectance curves of the heated and unheated sample mixtures were automatically scanned from 400 to 700 $m\mu$ by the instrument In all cases, K_2SO_4 was used as the reference material

RESULTS AND DISCUSSION

Thermogravimetric analysis (TGA) studies The TGA curves for the complexes are given in Fig 1

In general, the curves obtained corresponded to that expected for various dehydration and deamination reactions The compound, $[Cu(en)_3]SO_4$ (Fig 1/A), began to lose weight at about 200° The first weight-loss, which resulted in a break in the curve at 275°, approximated that for the loss of one ethylenediamine per mole of complex (Found, 15 6%, Theor 17 68%) The second weight-loss, resulting in the curve break at 295°, approximated that for the loss of two ethylenediamines (Found, 33 6%, Theor 35 36%) per mole of complex However, the compositions may be entirely fortuitous since no compounds were actually isolated during the thermal dissociation process On further heating, the last co-ordinated molecule of ethylenediamine was evolved, as well as the dissociation of the sulphate ion, resulting in a residue of copper (II) oxide

---

[17] W W WENDLANDT, T D GEORGE and G R HORTON, *J Inorg Nucl Chem* **17**, 173 (1961)

[18] W W WENDLANDT, *Analyt Chim Acta* **27**, 309 (1962)

[19] W W WENDLANDT, P H FRANKE and J P SMITH, *Analyt Chem* **35**, 105 (1963)

The compound, $[Cu(en)_2]SO_4$ (Fig 1/B), began to lose weight at about 280° This first weight loss, resulting in a curve break at about 340°, was due to the evolution of two moles of ethylenediamines (Found, 40 6%, Theor 42 96%) per mole of complex The loss of the two ethylenedeamines was then followed by the dissociation of the anhydrous copper sulphate, giving copper (II) oxide with perhaps a small amount of free copper as the residue The free copper oxidized on further heating, causing the increase in weight at higher temperatures There was no evidence for the existence of the monoamine complex Thus, the decomposition sequence is probably

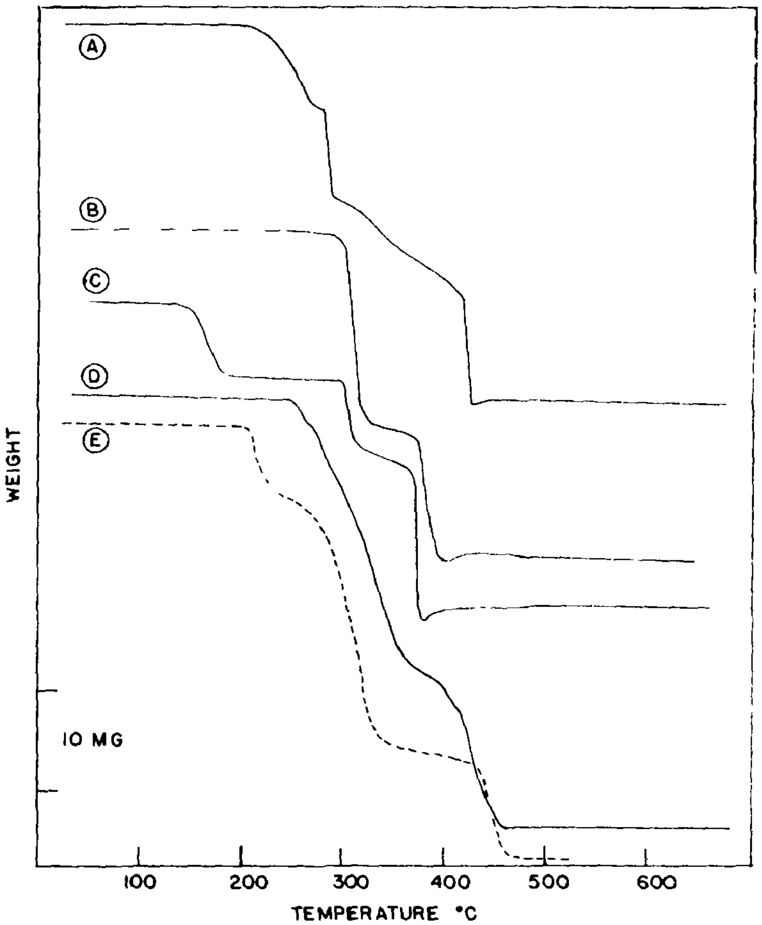


FIG 1 — Thermobalance curves of copper complexes
A $[Cu(en)_3]SO_4$, B $[Cu(en)_2]SO_4$, C $[Cu(en)(H_2O)_2]SO_4$ D $[Cu(pn)_2]SO_4$,
E $[Cu(tm)_2]SO_4$.

$$[Cu(en)_2]SO_4 \xrightarrow{280°} CuSO_4 + en + \text{decomposition products}$$

and

$$CuSO_4 \xrightarrow{390°} CuO + SO_3$$

The compound, $Cu(en)(H_2O)_2\ SO_4$ (Fig 1/C), began to lose weight at about 130°, resulting in an almost horizontal weight level from 190° to 300° This first weight-loss was due to the evolution of the two moles of water (Found, 14 4%. Theor 14 09%) per mole of complex Further dissociation then took place, above 300°, resulting in a copper copper oxide mixture at 380° Further heating caused oxidation of the free copper to give a residue of copper oxide The decomposition sequence for this complex is

$$[Cu(en)(H_2O)_2]SO_4 \xrightarrow{130^\circ} [Cu(en)]SO_4 + 2H_2O$$

$$[Cu(en)]SO_4 \xrightarrow{300^\circ} CuO + \textit{decomposition products}$$

The decomposition of $[Cu(pn)_2]SO_4$ (Fig 1/D) and $[Cu(tm)_2]SO_4$ (Fig 1/D) was similar to that described for $[Cu(en)_2]SO_4$ except that the decomposition temperatures were somewhat lower The minimum weight-loss temperatures were 250° and 200°, respectively In comparing the *bis*(amine) complexes, the order of decreasing thermal stability was

$$[Cu(en)_2]SO_4 > [Cu(pn)_2]SO_4 > [Cu(tm)_2]SO_4.$$

Differential thermal analysis (DTA) studies The DTA curves for the complexes are given in Figs 2 and 3 while the corresponding gas evolution (GE) curves are given in Figs 3 and 4

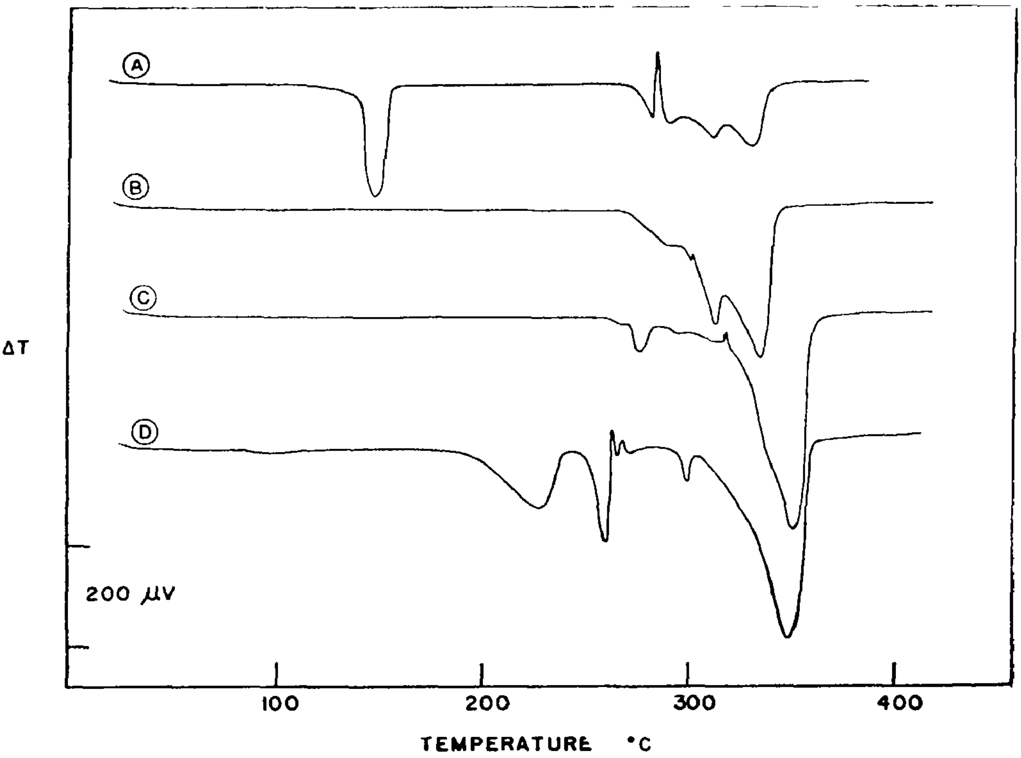


FIG 2 —Differential thermal analysis curves of copper complexes
A $[Cu(en)(H_2O)_2]SO_4$, B $[Cu(pn)_2]SO_4$, C $[Cu(en)_2]SO_4$, D $[Cu(en)_3]SO_4$

In comparing the DTA and GE curves, any thermal effect which appears in the DTA curve that is caused by the evolution of a volatile product will give rise to a GE peak also Some thermal effects, such as those due to a phase change of some type or a rearrangement reaction, in which a volatile product is not evolved, will not give a GE peak Thus, it is possible to distinguish between the various types of reactions found in the DTA curve.

The reactions found in the DTA curves corresponded, of course, to those previously found in the TGA curves The complex, $[Cu(en)(H_2O)_2]SO_4$ (Fig 2/A), gave an endothermic peak with a peak maxima temperature at 150°, which corresponded to the loss of the two co-ordinated waters Beginning at 275°, the ethylenediamine was evolved as evidenced by a broad endothermic peak Apparently, the deamination reaction is not as simple as would be expected since a sharp exothermic peak was observed at 285° The origin of this peak is unknown, but from the GE curve it is seen that there was a decrease in the GE peak at this temperature This would indicate that the origin of this peak is a rearrangement reaction or crystalline transition of some type The probable dissociation process involves the initial loss of a small amount of ethylenediamine, followed by a solid state rearrangement, then further deamination of the rearranged complex to give a residue of copper oxide This rather interesting phenomenon was not observed in the *bis*- or *tris*(ethylenediamine) complexes due perhaps to simultaneous endothermic reactions

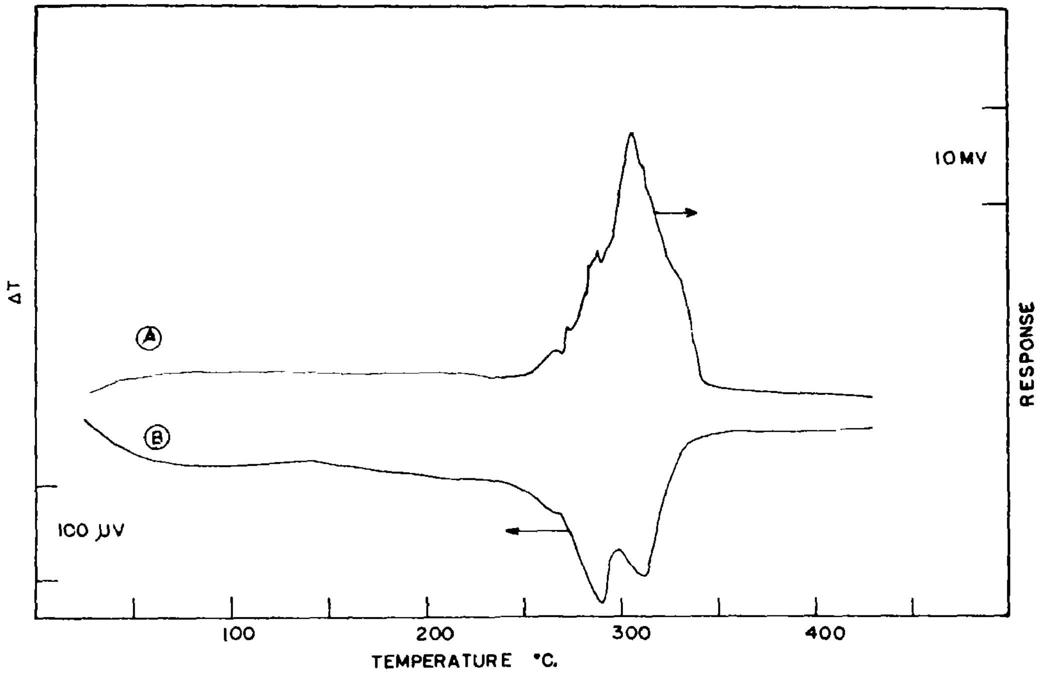


FIG. 3 —Differential thermal analysis and gas evolution curves of $[Cu(tm)_2]SO_4$

The compound, $[Cu(en)_3]SO_4$ (Fig 2/D), gave endothermic peaks at 225° and 260° which were due to the evolution of one mole of ethylenediamines per mole of complex as described under the TGA studies The remaining peaks, at 300° and 350°, respectively, were probably due to the total disruption of the *bis*(ethylenediamine) complex However, there is no unequivocal evidence that the *bis*(ethylenediamine) complex is formed since the remainder of the DTA is similar but not identical to that obtained for $[Cu(en)_2]SO_4$ (Fig 2/C) Reflectance studies, as will be seen, do not support the formation of the *bis*-complex intermediate The *bis*-(1,2-propanediamine) (Fig 2/B) and 1,3-propanediamine (Fig 3/B) complexes gave similar DTA curves. Each had two endothermic peaks in the 250 350° temperature range

The simultaneous gas evolution curves showed that except for the exothermic peak in the $[Cu(en)(H_2O)_2]SO_4$ DTA curve, all of the DTA peaks were caused by a reaction involving a gaseous decomposition product There was a slight temperature lag between the gas evolution curves and the DTA curves which was caused by the diffusion of the gaseous decomposition products through the sample residue before being swept through the furnace by the helium gas stream into the thermal conductivity detector

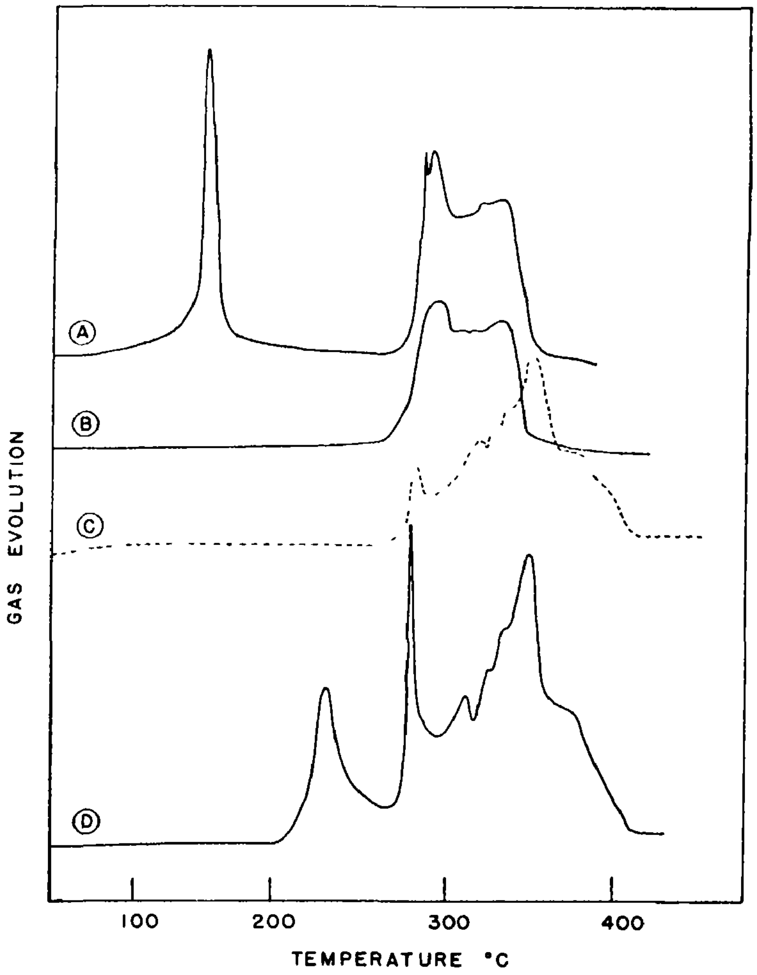


FIG 4 —Gas evolution curves of copper complexes
A $[Cu(en)(H_2O)_2]SO_4$, B $[Cu(pn)_2]SO_4$, C $[Cu(en)_2]SO_4$, D $[Cu(en)_3]SO_4$

Kinetics of the deaquation of $[Cu(en)(H_2O)_2]SO_4$ The activation energy, E_a, was determined for the deaquation reaction

$$[Cu(en)(H_2O)_2]SO_4(s) \rightarrow [Cu(en)]SO_4(s) + 2H_2O(g)$$

by a DTA method This method is based upon the relationship,

$$k = \frac{C_p\left(\dfrac{d\Delta T}{dt}\right) + K\Delta T}{K(A - a) + C_p\Delta T}$$

as originally derived by BORCHARDT and DANIELS,[20] where k is the rate constant, K is the constant characteristic of the apparatus, A is the total peak area, C_p is the total

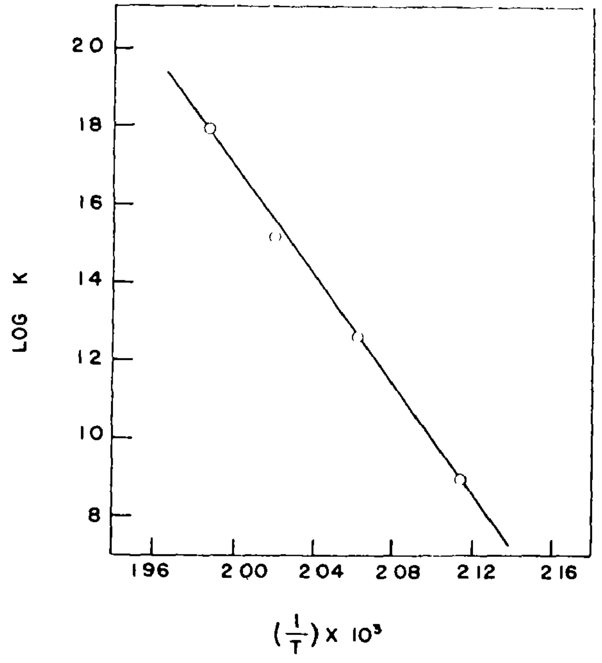


FIG. 5 Arrhenius plot for $[Cu(en)(H_2O)_2]SO_4$

heat capacity of the reactant or reference material, ΔT is the differential temperature, t is the time, and a is the area of the peak up to time t Assuming first order reaction kinetics and since C_p is normally quite small, the above equation was reduced to[21 23]

$$k = \frac{\Delta T}{A - a}$$

Calculations, made on the deaquation peak of $[Cu(en)(H_2O)_2]SO_4$ (Fig 2/A), gave the Arrhenius plot in Fig 5 The first order reaction kinetics assumption appears to be valid in this case as was confirmed by the asymmetry of peak [24] From the slope of the curve, an E_a of 29 kcal mole $^{-1}$ was obtained Although no great accuracy is claimed for this value, it does appear to be reasonable It was not possible to calculate

---

[20] H J BORCHARDT and F DANIELS, *J Amer Chem Soc* **79**, 41 (1957)

[21] V M PADMANABLAN, S C SARAIYA and A K SUNDARAM, *J Inorg Nucl Chem* **12**, 356 (1960)

[22] R P AGARWALA and M C NAIK, *Analyt Chim Acta* **24**, 128 (1960)

[23] W W WENDLANDT, *J Chem Educ* **38**, 571 (1961)

[24] H E KISSINGER, *Analyt Chem* **29**, 1703 (1957)

E_a for the other reactions because of the presence of multiple peak maximas in their DTA curves

Reflectance spectra studies The reflectance curves for the complexes are given in Figs 6 and 7

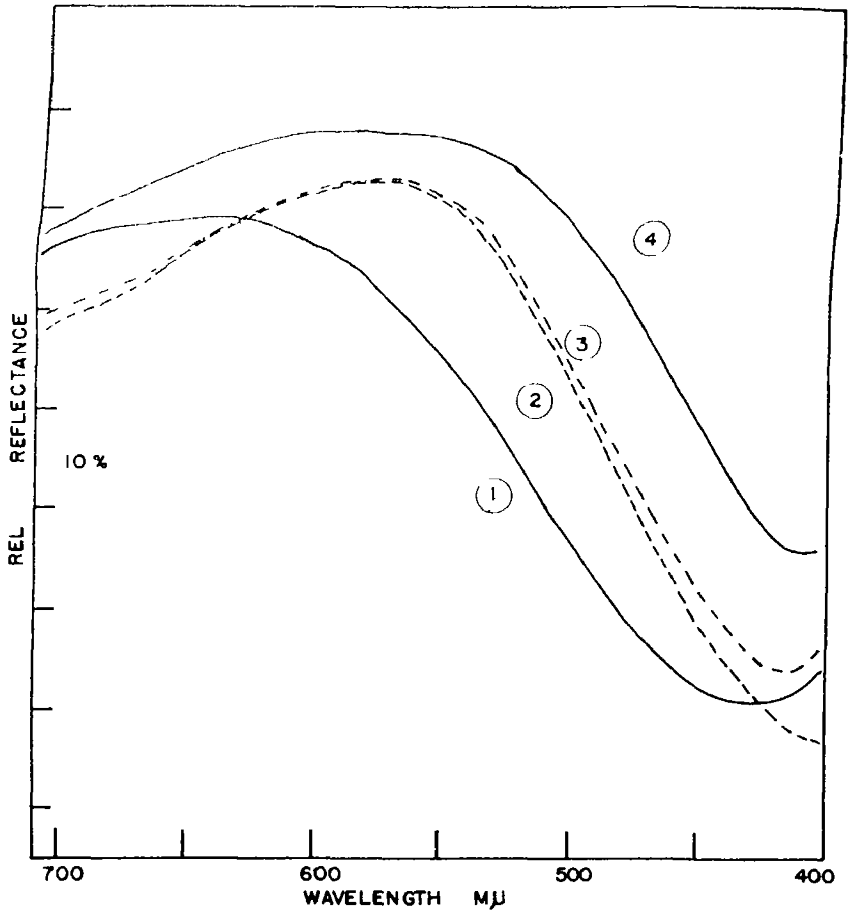


FIG 6 —Reflectance curves of copper complexes Curves are of 20% mixtures in K_2SO_4 at 25°, K_2SO_4 as reference
1 $[Cu(en)_3]SO_4$, 2 $[Cu(en)_2]SO_4$, 3 $[Cu(pn)_2]SO_4$, 4 $[Cu(tm)_2]SO_4$

The reflectance curves of the sample-potassium sulphate mixtures, at both ambient and elevated temperatures, were characterized by broad peaks These broad peaks, plus the limitation of the instrument to the 400–700 mμ range, prevented an accurate determination of peak maxima wavelengths However, for the curves in which this was possible, the following reflectance curve peak maximas were estimated

$[Cu(en)_3]SO_4$, 640 mμ, $[Cu(en)_2]SO_4$, 580 mμ, $[Cu(pn)_2]SO_4$, 570 mμ, and $[Cu(tm)_2]SO_4$, 580 mμ From solution absorption spectra studies, $[Cu(en)_2]^{++}$ has a peak at 550 mμ while $[Cu(en)_3]^{2+}$ has a peak at 610 mμ (25)

On heating a 20% $[Cu(en)(H_2O)_2]SO_4$–80% K_2SO_4 mixture, the curves in Fig 7 were obtained It is seen that the reflectance of the peak shifted to higher values as the

(25) E A TOMIC and J L BERNARD, *Analyt Chem* **34**, 632 (1962)

perature was increased as well as the peak shifting to shorter wavelengths The ly compositional change in the complex was the loss of water and perhaps re-cement of the water by sulphate ions From the curve it is seen that no loss of ordinated water took place below 100°, however, the dehydration process was ompleted between 150° and 170° which was in good agreement with the TGA curve.

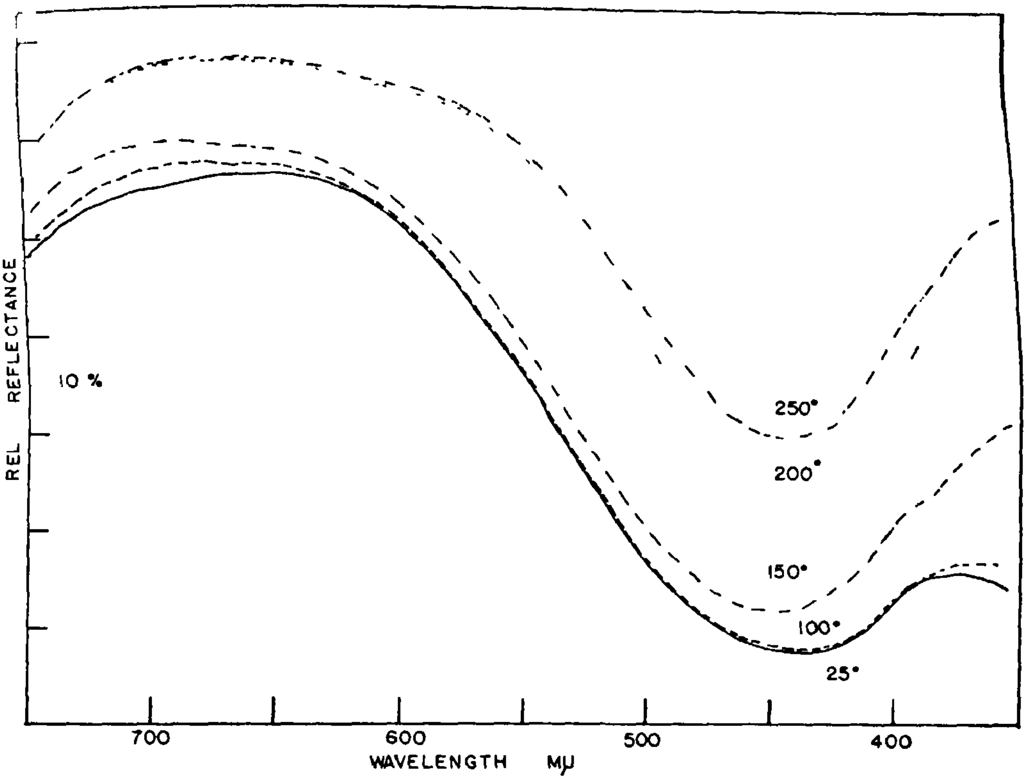


Fig. 7 —Reflectance curves of $[Cu(en)(H_2O)_2]SO_4$, 20 per cent mixture in K_2SO_4, at elevated temperatures

Attempts were made to obtain the reflectance curves of $[Cu(en)_3]SO_4$ as it was heated but they were unsuccessful due to the formation of a brown coloration on the surface of the sample Likewise, there was no evidence for the formation of the mono-(ethylenediamine) complex when the *bis*(ethylenediamine) complex was heated

General The relationship between the minimum weight-loss temperature and the coordinated amine ligand for a number of complexes is given in Fig 8

It can be seen that the thermal stability of the complexes decreased, with change in ligand, in the order en > pn > tm This relationship appears to be a general one for a number of complexes containing Cu(II), Co(III), and Pt(IV) as the central metal ions In each case, the complexes contained the same anion since changing the anion also has a pronounced effect on the thermal stability of the complex (26–29) Not

---

(26) T D George and W W Wendlandt, *J Inorg Nucl Chem* In press

(27) T D O'Brien and J C Bailar, *J Amer Chem Soc* **67**, 1856 (1945)

(28) J L Bear and W W Wendlandt, *J Inorg Nucl Chem* **17**, 286 (1961)

(29) W W Wendlandt, *Tex J Sci* **14**, 264 (1962)

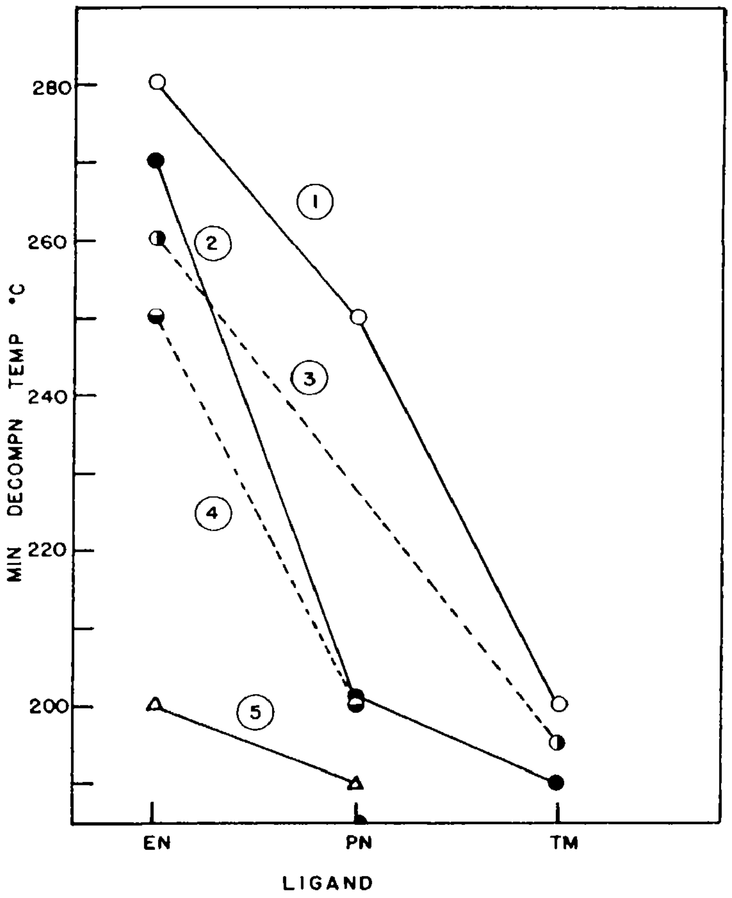


FIG 8 —Relationship between thermal stability and the coordinated amine ligand of some metal complexes

1 $[\mathrm{Cu(amine)_2}]\mathrm{SO_4}$, 2 $[\mathrm{Co(amine)_2CO_3}]\mathrm{Cl}$(30), 3 $[\mathrm{Co(amine)_3}]\mathrm{Cl_3}$(30), 4 $[\mathrm{Pt(amine)_3}]\mathrm{Br_4}$(29), 5 $[\mathrm{Pt(amine)_2}]\mathrm{Cl_2}$(29)

enough information is available, as yet, to correlate the decomposition temperatures of the amine complexes with the type of central metal ion present This will have to be done with complexes containing the same number of coordinated ligand groups, the same central metal ion oxidation state, the same anion, and identical experimental conditions

Acknowledgement -This work was sponsored by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, through Contract No AF AFOSR 23 63 The helpful assistance of T D GEORGE and P H FRANKE, JR , is gratefully acknowledged

(30) W W WENDLANDT, T D GEORGE and K V KRISHNAMURTY, *J Inorg Nucl Chem* **21,** 69 (1961)

J Inorg Nucl Chem 1963 Vol 25 pp 843 to 850 Pergamon Press Ltd Printed in Northern Ireland

THERMAL DECOMPOSITION OF METAL COMPLEXES—V

SOME HALOPENTAMMINECOBALT (III) HALIDE COMPLEXES(1)

W W Wendlandt and J P Smith
AFOSR Centre for Molecular Research Department of Chemistry
Texas Technological College, Lubbock, Texas

(*Received* 8 *November* 1962)

Abstract The thermal dissociation of nine halopentamminecobalt (III) complexes was studied by the techniques of thermogravimetry (*in vacuo*), differential thermal analysis (in helium) and gas evolution analysis (in helium) The stoicheiometry of the dissociation reactions was determined by analysis of the residues and reaction products Activation energies for the dissociation of several of the complexes were also obtained

The complexes dissociated by two different mechanisms (a) those in which the Co(III) was reduced by iodide ion, and (b) those in which the Co(III) was reduced by ammonia In the latter case ammonium halide and nitrogen were also obtained in the reaction products

The thermal dissociation of a number of anionopentamminecobalt (III) complexes has previously been studied The compounds investigated were $[Co(NH_3)_5Cl]Cl_2$ from the thermal dissociation of $[Co(NH_3)_6]Cl_3$,(2,3) $[Co(NH_3)_5N_3]X_n$ (where X = various monovalent and divalent anions),(4) $[Co(NH_3)_5(NO_2)](NO_2)_2$,(5), formato- acetato- and propionato-pentammine cobalt (III) nitrates,(6) and $[Co(NH_3)_5N_3](N_3)_2$ (7) However, only in several cases have the dissociation reactions been studied in any great detail (3,7)

It is thus the object of this investigation to study the thermal dissociation of complexes of the type, $[Co(NH_3)_5Y]X_2$, where X and Y are Cl Br$^-$, and I The thermal dissociation reactions were studied by thermogravimetry (*in vacuo*), differential thermal analysis-gas evolution analysis (in helium), and by product analysis (in helium and *in vacuo*)

EXPERIMENTAL

Preparation of metal complexes $[CO(NH_3)_5Cl]Cl_2$ and $[CO(NH_3)_5Br]Br_2$ were prepared by heating the corresponding aquopentammine-cobalt (III) complexes at 110 for 4 hr The latter compounds were prepared as previously described (8)

The $[Co(MH_3)_5I]X_2$ compounds were prepared as previously described (9) $[Co(NH_3)_5Cl]Br_2$ and $[Co(NH_3)_5Br]Cl_2$ were prepared by treating $[Co(NH_3)_5Cl]Cl_2$ and $[Co(NH_3)_5Br]Br_2$ with cold concentrated HBr and HCl, respectively (10) $[Co(NH_3)_5Cl]I_2$ and $[Co(NH_3)_5Br]I_2$ were prepared by reacting $[Co(NH_3)_5Cl]Cl_2$ and $[Co(NH_3)_5Br]Br_2$ respectively with a cold saturated solution of KI (11)

---

(1) For Part (IV) see W W Wendlandt *J Inorg Nucl Chem* **25**, 833 (1963)

(2) W Biltz, *Z Anorg Chem* **83**, 177 (1913)

(3) G L Clark, A J Quick and W D Harkins, *J Amer Chem Soc* **42**, 2496 (1920)

(4) M Linhard and H Flygare, *Z Anorg Chem* **262**, 328 (1950)

(5) N I Lobanov, I S Rassonskaya and A V Ablov, *Zh Neorg Khim* **3**, 1355 (1958)

(6) M Figlarz, *C R Acad Sci Paris*, **249**, 2780 (1959)

(7) T B Joyner and F H Verhoek, *J Amer Chem Soc* **83**, 1069 (1961)

(8) F Basolo and R K Murmann *Inorganic Synthesis*, Vol 4, p 171 (Edited by J C Bailar) McGraw-Hill, New York (1953)

(9) R G Yalman *J Amer Chem Soc* **77**, 3219 (1955)

(10) S M Jorgensen, *J Prakt Chem* **19**, 49 (1879)

(11) F Ephraim, *Dtsch Chem Ges Ber* **56**, 1531 (1923)

The [illegible] salts were analysed for cobalt, by ignition in air at 800 and weighing as Co_3O_4, and [illegible] Kjeldahl method The results of the analyses are given in Table 1

TABLE 1 ANALYTICAL DATA FOR COBALT COMPLEXES

Compound	Cobalt (%) Theoretical	Cobalt (%) Found	Ammonia (%) Theoretical	Ammonia (%) Found
$[Co(NH_3)_5Cl]Cl_2$	23 53	23 1	34 00	33 4
$[Co(NH_3)_5Cl]Br_2$	17 37	17 6	25 09	25 1
$[Co(NH_3)_5Br]Br_2$	15 35	15 8	22 18	22 2
$[Co(NH_3)_5Br]Cl_2$	19 98	19 9	28 87	28 9
$[Co(NH_3)_5Br]I_2$	12 33	12 3	17 82	17 9
$[Co(NH_3)_5Cl]I_2$	13 60	13 6	19 65	19 6
$[Co(NH_3)_5I]I_2$	11 23	11 3	16 22	15 8
$[Co(NH_3)_5I]Br_2$	13 68	13 6	19 76	19 4
$[Co(NH_3)_5I]Cl_2$	17 23	17 2	24 90	24 9

Thermobalance The automatic recording vacuum thermobalance has previously been described (12) Sample sizes ranged in weight from 15–20 mg and were pyrolysed at a furnace heating rate of about 5 per min The pressure inside the balance during the pyrolysis ranged from 20 to 40 μ The voltage signals corresponding to the temperature and sample weight were recorded as a function of time on a two-pen strip-chart potentiometric recorder

Differential thermal analysis-gas evolution apparatus The apparatus has previously been described (13) Sample sizes ranged in weight from 30 40 mg and were pyrolysed in a dynamic helium atmosphere at a furnace heating rate of 10° per min The voltage signals corresponding to the differential temperature and the gas evolution of the sample were recorded as a function of the furnace temperature on two X–Y recorders

Pyrolysis product analysis The pyrolysis apparatus consisted of a Vycor tube furnace, a "cold finger" trap, and a "U"-tube filled with anhydrous $Mg(ClO_4)_2$ About 200 300 mg of the sample, contained in a small tarred porcelain boat, was placed in the tube furnace Pyrolysis of the sample, at a heating rate of about 10° per min, was carried out in a slow stream of dry helium gas The pyrolysis solids, such as NH_4X, were collected on the "cold finger" and identified qualitatively by tests for NH_4 and halide ions The liberated iodine, in those compounds containing iodine, which was also condensed by the "cold finger", was dissolved in dilute KI solution and titrated with standard $Na_2S_2O_3$ solution The pyrolysis residue was analysed by (a) direct weighing, (b) heating in air and weighing as Co_3O_4, and (c) dissolving in water, adding an excess of standard $AgNO_3$ solution, filtering, and back-titrating with a standard KCNS solution From (b) and (c) the ratio, X/Co, was determined

The nitrogen in the pyrolysis products was determined by using a modified Dumas nitrogen method in which a portion of the Dumas tube was filled with anhydrous $Mg(ClO_4)_2$ to absorb the evolved ammonia Pyrolysis of the sample, at a heating rate of about 10° per min, was carried out in the tube *in vacuo* The evolved ammonia was absorbed on the $Mg(ClO_4)_2$ while the nitrogen content was determined by flushing the cooled tube with carbon dioxide and collecting the nitrogen over KOH in an azotometer The nitrogen in the decomposition gases was also qualitatively detected, in separate experiments, by the use of a gas chromatograph and a mass spectrometer

RESULTS AND DISCUSSION

Weight-loss studies The weight-loss curves of the halopentamminecobalt complexes are given in Figs 1 and 2

---

(12) T D GEORGE and W W WENDLANDT, *J Inorg Nucl Chem* In press

(13) W W WENDLANDT, *Anal Chim Acta* **27**, 309 (1962)

All of the complexes, except perhaps $[Co(NH_3)_5I]I_2$ and $[Co(NH_3)_5Br]I_2$, decom- ed in a single step as shown by the continuous weight-loss of the compound down o a residue of CoX_2 The order of decreasing thermal stability, along with minimum ight-loss temperatures, was $[Co(NH_3)_5Cl]Cl_2$, 150° $[Co(NH_3)_5Cl]Br_2$, 138° $>$ Co(NH_3)_5Br]Cl_2$ 110° $>$ $[Co(NH_3)_5Br]Br_2$, 100° $[Co(NH_3)_5I]Cl_2$, 50° = $[Co(NH_3$ I]I_2$, 50° $>$ $[Co(NH_3)_5Br]I_2$, 40° $[Co(NH_3)_5Cl]I_2$, 40° $[Co(NH_3)_5I]Br_2$, 35° The

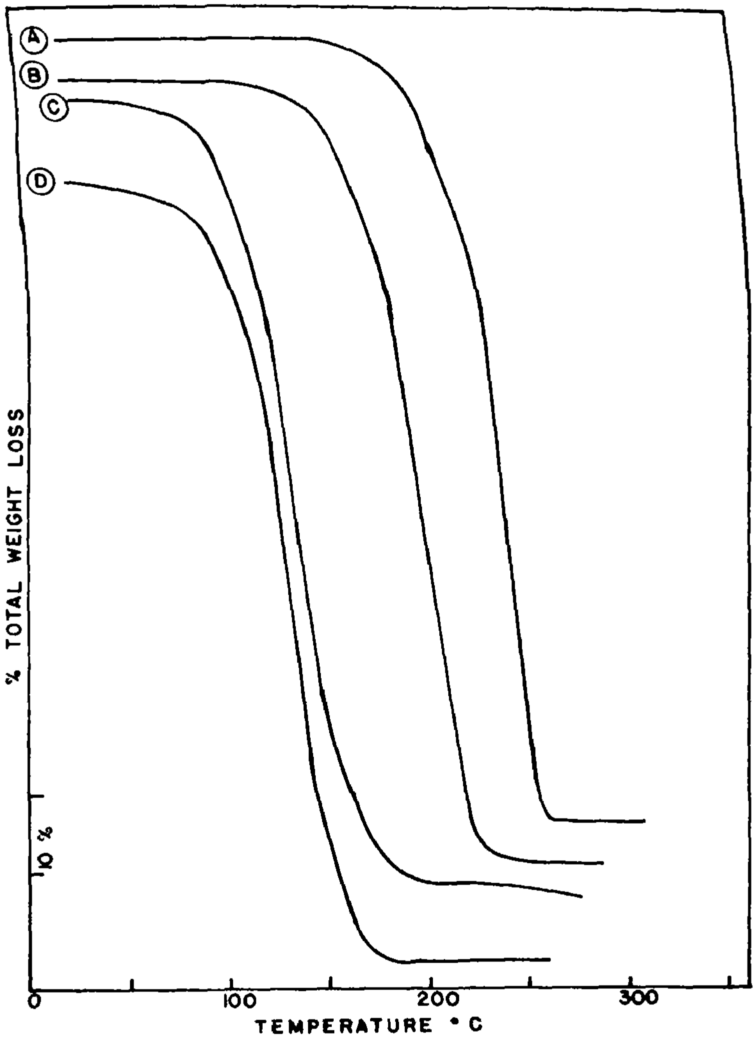


Fig. 1 - Weight-loss curves for cobalt complexes *in vacuo*
$[Co(NH_3)_5X]Y_2$
A Cl]Cl$_2$ B Br]Cl$_2$, C I]Cl$_2$ D I]Br$_2$

complexes containing iodine, either in the co-ordination or ionic spheres, were certainly the least stable This was perhaps due to the ease of oxidation of the iodide ion to free iodine Free iodine was evolved in the reactions as determined by the product analysis studies

Since a single step decomposition reaction was indicated by the weight-loss curves, the kinetics for several of the reactions were calculated by the method of FREEMAN and

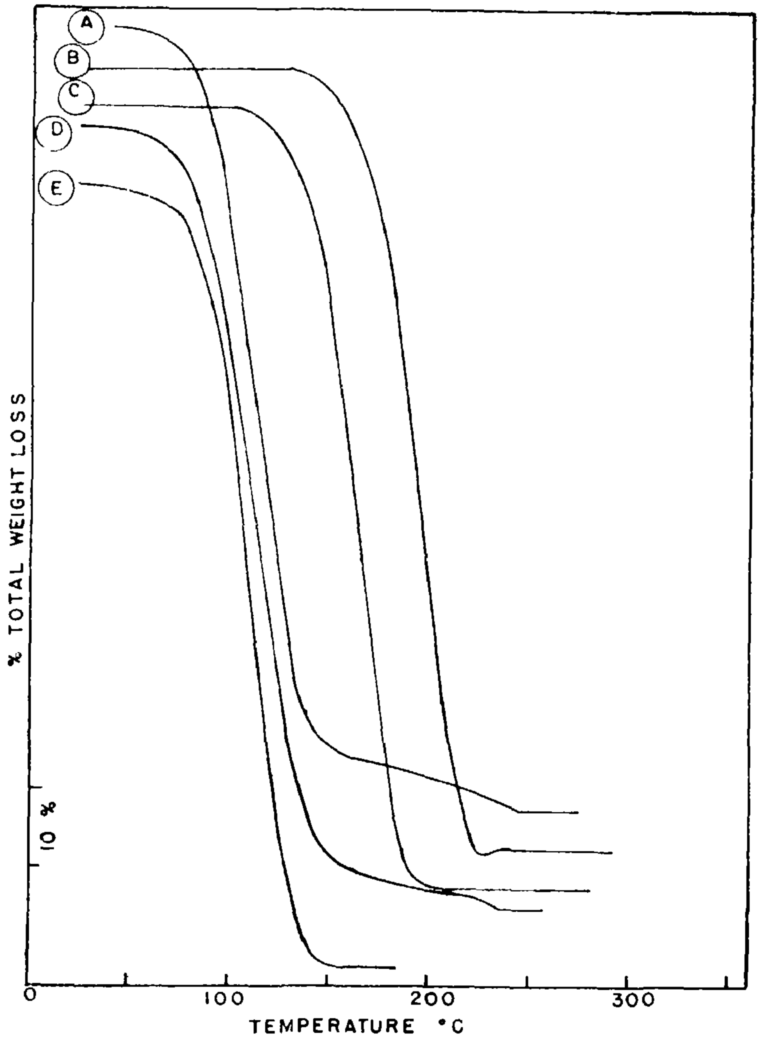


Fig 2 Weight-loss curves for cobalt complexes *in vacuo* $[Co(NH_3)_5X]Y_2$
A $I]I_2$ B $Cl]Br_2$ C $Br]Br_2$ D $Br]I_2$ E $Cl]I_2$

Carroll[11] A straight line relationship was only obtained for the complexes containing bromine and chlorine These kinetics plots are shown in Fig 3 The order of reaction and the activation energy, in kcal, so obtained were $[Co(NH_3)_5Cl]Cl_2$ 0 7 28, $[Co(NH_3)_5Br]Br_2$, 0 9, 21, $[Co(NH_3)_5Cl]Br_2$, 1 2, 21, and $[Co(NH_3)_5Br]Cl_2$, 1 2, 25 These kinetics data are for the reactions described in the product analysis studies The activation energies obtained were so similar and involved considerable experimental error that the slight differences obtained could hardly be ascribed to an anion effect

An explanation is not known for the poor results obtained for the iodine complexes The thermal dissociation reaction for these compounds is probably complicated by the liberation of free iodine so that several simultaneous reactions are taking place instead of a single reaction

---

[11] E S Freeman and B Carroll, *J Phys Chem* **62**, 394 (1958)

Differential thermal analysis-gas evolution studies The differential thermal analysis (DTA) curves are given in Fig 4 while the gas evolution (GE) curves are given in Fig 5

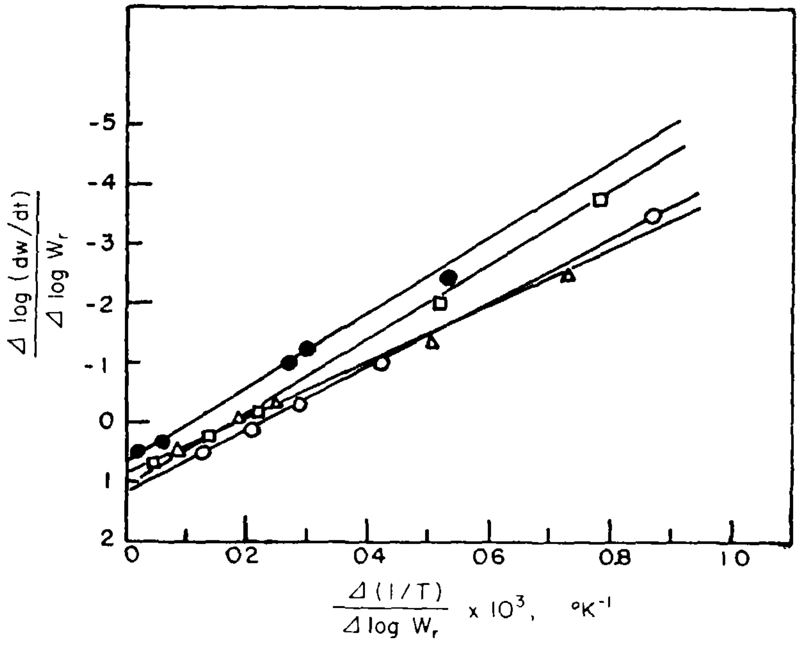


FIG 3 — Kinetics plots for the thermal dissociation of some cobalt complexes $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_5Cl]Br_2$, $[Co(NH_3)_5Br]Cl_2$ $[Co(NH_3)_5Br]Br_2$

All of the DTA curves were characterized by a large endothermic peak followed either by a smaller peak or else a shoulder peak The main dissociation reaction probably took place during the first endothermic peak followed by a slower reaction such as the sublimation of some of the reaction products, such as NH_4X or free iodine The decomposition mechanism appears to be different in helium than *in vacuo* since the weight-loss curves showed a continuous loss in weight It should also be observed that the minimum decomposition temperatures were higher in helium than those obtained by TGA *in vacuo* Two explanations are offered for this behaviour (a) a higher heating rate, 10 per min in helium *versus* 5 per min *in vacuo*, and (b) since a gaseous component is evolved, the decomposition temperatures are pressure dependent The thermal stability in helium, as determined by the minimum temperature at which ΔT deviated from the base line, was $[Co(NH_3)_5X]Y_2$ where X and Y are, $Cl]Cl_2$, 205° $Cl]Br_2$, 190 $Br]Cl_2$, 190° $Br]Br_2$, 160 $I]Cl_2$, 150° $I]I_2$, 145° $I]Br_2$, 140 $Br]I_2$ 120° $Cl]I_2$ 115°

The gas evolution curves were similar, but inverted, to the DTA curves obtained for a given compound. This indicated that for all of the endothermic peaks a gaseous product was evolved and that there were no detectable phase transitions which did not involve a gaseous product Again, the curves indicated that the main dissociation reaction occurred during the first peak

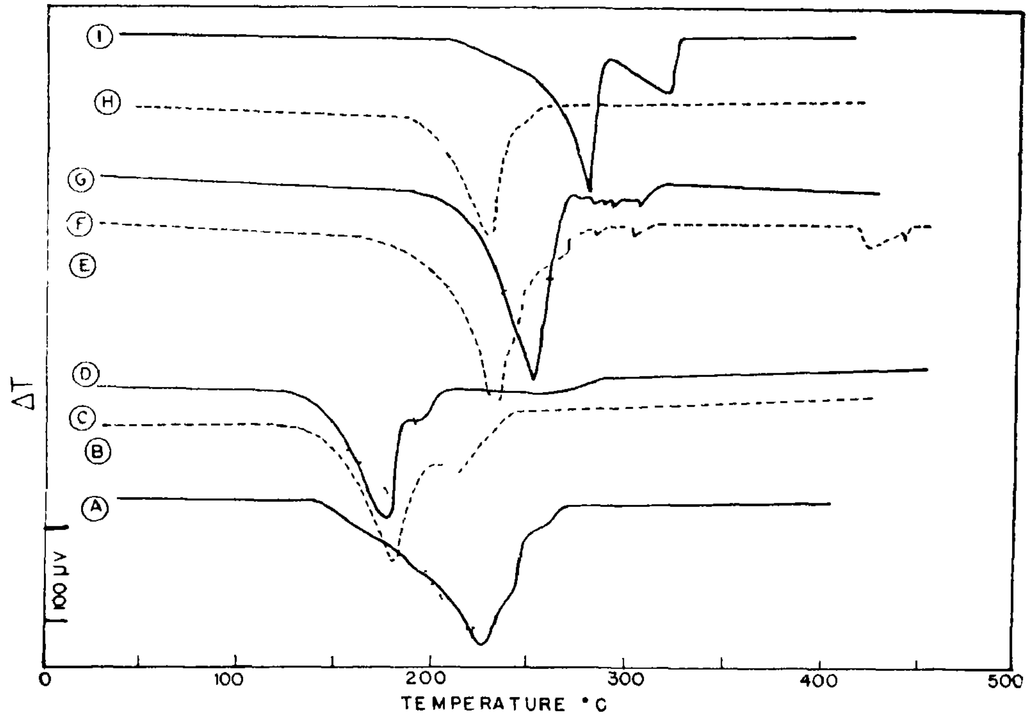


FIG. 4 — Differential thermal analysis curves of cobalt complexes in helium $[Co(NH_3)_5X]Y_2$
A I]Br_2, B I]Cl_2, C Cl]I_2, D Br]I_2, E I]I_2, F Br]Br_2, G Br]Cl_2
H Cl]Br_2, I Cl]Cl_2

Product analysis studies stoichiometry of reaction The results of the product analyses are given in Table 2

The data agreed well with the following dissociation reactions

$$6[Co(NH_3)_5Cl]Cl_2 \rightarrow 6CoCl_2 + 6NH_4Cl + 22NH_3 + N_2$$

$$6[Co(NH_3)_5Cl]Br_2 \rightarrow 6CoBr_2 + 6NH_4Cl + 22NH_3 + N_2$$

$$6[Co(NH_3)_5Br]Br_2 \rightarrow 6CoBr_2 + 6NH_4Br + 22NH_3 + N_2$$

$$6[Co(NH_3)_5Br]Cl_2 \rightarrow 6CoCl_2 + 6NH_4Br + 22NH_3 + N_2$$

and those for complexes containing iodine

$$2[Co(NH_3)_5Br]I_2 \rightarrow CoBr_2 + CoI_2 + I_2 + 10NH_3$$

$$2[Co(NH_3)_5Cl]I_2 \rightarrow CoCl_2 + CoI_2 + I_2 + 10NH_3$$

$$2[Co(NH_3)_5I]I_2 \rightarrow 2CoI_2 + I_2 + 10NH_3$$

$$2[Co(NH_3)_5I]Br_2 \rightarrow 2CoBr_2 + I_2 + 10NH_3$$

$$2[Co(NH_3)_5I]Cl_2 \rightarrow 2ClCo_2 + I_2 + 10NH_3$$

The dissociation mechanism is different for these complexes containing iodine, mainly from the standpoint of the Co(III) → Co(II) reduction In iodine containing

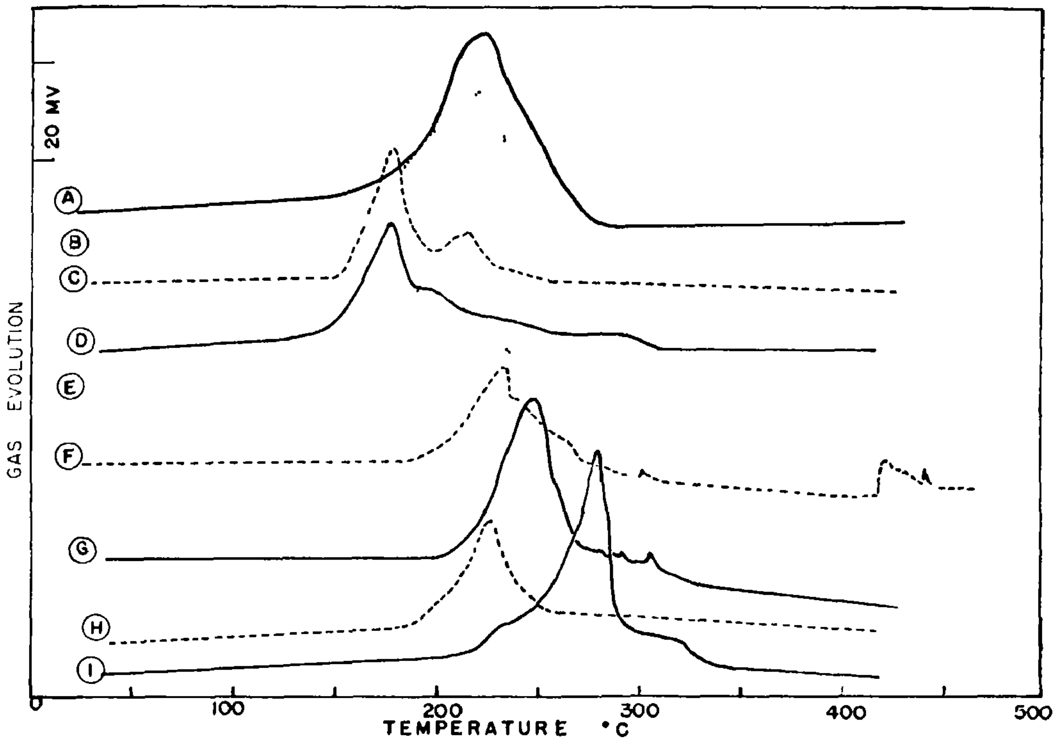


Fig 5 Gas evolution curves of cobalt complexes in helium $[Co(NH_3)_5X]Y_2$
A I]Br_2, B I]Cl_2, C Cl]I_2, D Br]I_2, E I]I_2, F Br]Br_2, G Br]Cl_2
H Cl]Br_2, I Cl]Cl_2

TABLE 2—PRODUCT ANALYSIS DATA FOR COBALT COMPLEXES

Compound $[Co(NH_3)_5X]Y_2$	Residue Formula	Cobalt, (%)	X/Co	Sublimate		NH_3/Co	N_2/Co	I/Co
				Formula	Halide, (%)			
Cl]Cl_2	$CoCl_2$	45 4*	2	NH_4Cl	66 0*	3 59*	0 169*	
		45 38†			66 28†	3 67†	0 167†	
Cl]Br_2	$CoBr_2$	26 9	2	NH_4Cl	66 0	3 60	0 175	
		26 94						
Br]Br_2	$CoBr_2$	26 9	2	NH_4Br	83 0	3 68	0 169	
					81 58			
Br]Cl_2	$CoCl_2$	45 4	2	NH_4Br	82 4	3 64	0 167	
Br]I_2	CoIBr	22 2	2			5 00*		1 03*
		22 16				5 †		1 †
Cl]I_2	CoICl	26 7	2			4 97		1 02
		26 63						
I]I_2	CoI_2	18 8	2			4 75		1 00
		18 85						
I]Br_2	$CoBr_2$	27 0	2			4 96		0 98
I]Cl_2	$CoCl_2$	45 4	2			4 98		0 99

* Experimental values
† Theoretical values

complexes, the iodide ion is the reducing agent, forming Co(II) and free iodine. For the other complexes, ammonia is the reducing agent, giving Co(II) halide, ammonium halide and nitrogen. This latter case was identical to the results found for the hexamminecobalt (III) complexes.(15)

It should also be noted that the residue formed always contained the cobalt salt of the halogen in the ionization sphere (except for $[Co(NH_3)_5X]I_2$, X = Cl, Br) while the ammonium halide contained the halogen from the co-ordination sphere of the complex.

Acknowledgement—This work was supported by the U.S. Air Force Office of Scientific Research through Contract No. AF 49(638)-787.

---

(15) W. W. WENDLANDT, *J. Inorg. Nucl. Chem.* In press.

J. inorg. Nucl. Chem., 1963, Vol. 25, pp. 851 to 857. Pergamon Press Ltd. Printed in Northern Ireland

PYROLYSIS OF URANIUM COMPOUNDS—I

URANYL SULPHATE*

K. J. Notz† and H. H. Jaffé

University of Cincinnati, Cincinnati 21, Ohio

(*Received* 23 *July* 1962; *in revised form* 2 *January* 1963)

Abstract—The pyrolysis of $UO_2SO_4 \cdot 3H_2O$ was studied by means of differential thermal analysis (DTA) and thermogravimetric analysis (TGA). Dehydration occurred in three steps with the consecutive formation of the dihydrate, the monohydrate, and finally the anhydrous salt. At 755°, UO_2SO_4 undergoes an enantiotropic phase transition. The rate of decomposition of UO_2SO_4 to U_3O_8 was deduced to be limited by both nucleation and growth. The rate expression for this reaction, in terms of milligrams of weight lost per minute per square meter of active surface is: rate $= 1.1 \times 10^{11} \exp(-58{,}600/RT)$.

The study of pyrolysis reactions by a combination of thermogravimetric analysis (TGA) and differential thermal analysis (DTA) has gained widespread usage because of the efficacy of the combined methods. Application of this technique to the pyrolysis of uranyl sulphate trihydrate was effective in determining the various reactions which occur. In addition, the thermal decomposition of the anhydrous salt provided an interesting study in heterogeneous kinetics.

Preparation of $UO_2SO_4 \cdot 3H_2O$ *and* UO_2SO_4

Uranyl sulphate crystallizes from aqueous solution as the trihydrate $UO_2SO_4 \cdot 3H_2O$, at ordinary temperatures.(1) The dihydrate and monohydrate are also known.(1,2,3) Two crystalline forms of the trihydrate have been reported,(3,4) but apparently only one of these forms is stable when the crystals are grown under equilibrium conditions.(1) A $3\frac{1}{2}$ hydrate has also been reported.(5)

Uranyl sulphate hydrate (E. H. Sargent, C.P.), nominally the trihydrate but actually containing only 2.65 moles of water, was used as the starting material. Recrystallization from aqueous solution yielded a nearly stoicheiometric trihydrate (2.98 moles of water). The X-ray diffraction pattern of this material agreed with published data(6,7) for orthorhombic $UO_2SO_4 \cdot 3H_2O$.

Anhydrous uranyl sulphate was prepared by calcining pulverized trihydrate to constant weight at 500°. The weight loss observed corresponded to formation of UO_2SO_4. Analyses for uranium (by calcination to U_3O_8 in two steps—first at 900°, then at 750°) and sulphate (by precipitation as $BaSO_4$) gave these results. (Found, U, 64·89; SO_4. 26·39; Calc. U, 65·02, SO_4, 26·24%) X-ray diffraction data for UO_2SO_4, which have not been previously reported, are listed in Table 1 The surface area of this sample was determined as 0 81 m²/g by the BET method

---

* Based on a thesis submitted to the Graduate School of Arts and Sciences of the University of Cincinnati in partial fulfillment of the requirements for the degree of Master of Science in Chemistry.

† Present address: University of Miami, Coral Gables 46, Florida.

(1) C. H. Secoy, *J. Amer. Chem. Soc.* **70**, 3450 (1948).

(2) A. Colani, *Bull. Soc. chim.* **43**, 754 (1928).

(3) L. Levshin and G. D. Sheremet'ev, *J. Exptl. Theor. Phys. (USSR)*, **17**, 204 (1947).

(4) B. F. Gordon and A. M. Denisov, *Ukrain. Khim. Zhur.* **19**, 368 (1953).

(5) H. W. Dunn, U.S.A.E.C. Report ORNL-2092 (1956).

(6) R. J. Traill, *Amer. Mineralogist*, **37**, 394 (1952).

(7) ASTM X-Ray Powder Data File Card No. 8-191.

TABLE 1 —DIFFRACTION DATA FOR α-UO_2SO_4

Radiation CuKα, Nickel-filtered

Diffractometer 1 Divergence and scatter slits

0 003 in Receiving slit

½ min Scanning speed

Recorder 4 sec Time constant and scale factor of 4

2θ	d(Å)	$100\ I/I_0$	2θ	d(Å)	$100\ I/I_0$
13 50	6 57	20	35 86	2 503	15
14 30	6 19	15	38 35	2 347	10
17 30	5 12	40	40 40	2 232	5
20 60	4 42	60	41 20	2 191	5
21 10	4 21	100	42 90	2 108	5
21 85	4 06	10	43 50	2 080	10
26 85	3 32	20	45 58	1 990	10
27 13	3 28	25	46 5	1 953	10
27 70	3 22	10	47 2	1 926	20
28 73	3 10	20	47 6	1 910	10
31 20	2 866	5	48 9	1 863	5
31 40	2 848	10	49 7	1 835	15
31 85	2 809	15	51 6	1 771	10
32 80	2 731	20	54 5	1 683	5
33 60	2 667	10	56 5	1 629	5
34 60	2 593	10	Cut off		
34 93	2 569	15			

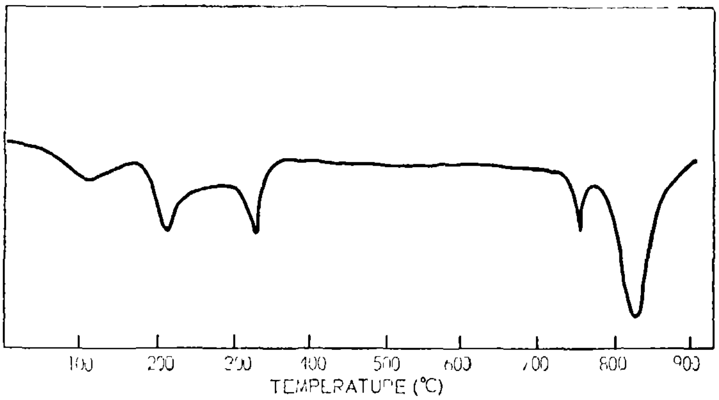


FIG 1 —DTA of UO_2SO_4 $3H_2O$

Differential thermal analysis (DTA)

DTA was performed with a commercial unit, the Deltatherm (Technical Equipment Corp , Denver) Precalcined alumina was used both as a reference material and as a sample diluent A heating rate of 10°/min and a recording sensitivity of 5°/in were employed

A DTA trace of UO_2SO_4 $3H_2O$ is shown in Fig 1 The recording shows three low perature endotherms, at 100°, 210° and 320°, a rather sharp transition at 755°, and ge endotherm at 825° It will be shown that these thermal effects are due to wise loss of hydrate water, with the successive formation of $UO_2SO_4 2H_2O$, $_2SO_4$ H_2O, and UO_2SO_4, an enantiotropic phase transition of UO_2SO_4 at 755°, nd finally decomposition to U_3O_8

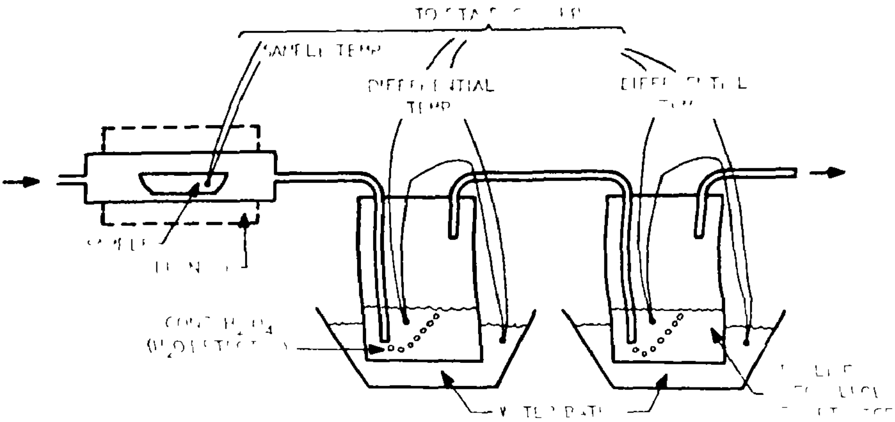


FIG. 2 - Equipment to detect evolution of water and oxygen

The decomposition gases given off during pyrolysis were analysed by a thermal method based on a principle suggested by Dr R E GRIM The gases were passed through absorbers which would selectively absorb H_2O (concentrated H_2SO_4) and oxygen (alkaline pyrogallol), with a resultant temperature change as a consequence of the absorption Oxygen absorption was used to detect loss of sulphate since this decomposition would yield either SO_2 plus oxygen or SO_3 which would in turn decompose because of the $SO_3 \rightleftarrows SO_2 + \frac{1}{2}O_2$ equilibrium, thus forming some oxygen The apparatus used is shown in Fig 2 The outputs from the thermocouples were fed to the recorder part of the Deltatherm The recording obtained was similar to a conventional DTA trace The sulphuric acid absorber gave three exothermic peaks at 110, 200 and 300, due to the evolution of water in three steps The areas under each peak were approximately equal, indicating that equal quantities of water are lost in each step The oxygen absorber showed only a single exotherm, at about 780 suggesting that sulphate decomposition occurred as a single reaction

Thermogravimetric analysis (TGA)

The automatic recording thermobalance used for TGA, and also for the kinetic work, has been described previously [8] Programmed temperatures were obtained by means of a gear-driven transformer A heating rate of 3°C per minute was employed The reaction tube was constantly flushed with helium during a run

The TGA curve obtained verified the stepwise loss of each mole of water of hydration, with the successive formation of the dihydrate, the monohydrate, and the anhydrous salt These reactions occurred at about 100, 200 and 300, respectively The intervening plateaus coincided with the calculated weights for the corresponding products

---

[8] K J NOTZ and M G MENDEL, *J Inorg Nucl Chem* **14**, 55 (1960)

Anhydrous uranyl sulphate was stable to about 600, then decomposed at a gradually increasing rate, finally yielding U_3O_8 at about 760 The reaction obviously occurred in one step, in agreement with the oxygen absorption experiment This then indicated that of the two DTA endotherms at 755 and 825, one must be due to a phase transition

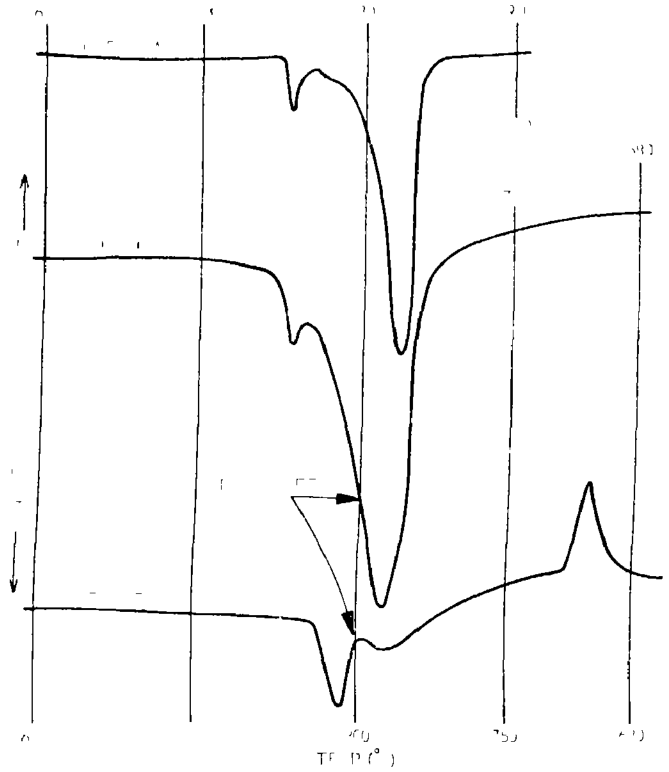


Fig. 3 Differential cooling curves of UO_2SO_4

Phase transition

Figure 3 shows two differential cooling curves (curves B and C) along with a conventional DTA trace (curve A) In the case of curves B and C, the heater power was turned off at the point indicated, and recording was continued while these samples cooled Both of these curves were obtained during a single run by utilizing two sample wells and two channels of the Deltatherm

Sample B was a conventionally diluted sample, as was sample A However, sample C was not diluted Since the thermal effects were endothermic, the greater quantity of material present in the C well caused curve C to lag behind curves A and B This permitted turning off the heater at a point where sample B had almost completed the second endotherm, but sample C had just completed the first endotherm Cooling curve B, where both endotherms had occurred, showed no thermal effects on cooling However, curve C, where only the first endotherm had occurred, exhibited a single exotherm on cooling This shows conclusively that the endotherm at 755° is due to a reversible phase change of UO_2SO_4, while the second endotherm is due to decomposition to U_3O_8 The difference in decomposition temperatures as determined by DTA

5) and TGA (about 700°) is due to the different ambient atmospheres. This nt has been discussed previously in greater detail in a note.[9]

Following standard methods of nomenclature, the low temperature form of nyl sulphate will be designated as α-UO$_2$SO$_4$ and the high temperature form as O$_2$SO$_4$. Similar phase transitions have been noted for any other sulphates.[10,11,12]

TABLE 2. KINETIC RUNS

Temperature (°C)	Reaction rate (mg/min per 400 mg)
639	1.756
655	3.091
670	5.027
689	9.480
704	15.21
721	25.83

Kinetics

Isothermal rate data were obtained by introducing a 400 mg sample of anhydrous UO$_2$SO$_4$ into the thermobalance at the desired temperature. Continuous weight and temperature recordings were started immediately. As soon as temperature equilibrium was established and isothermal control attained, the weight chart was marked to indicate that usable data were being recorded. The theoretical weight loss for conversion to U$_3$O$_8$ is 93.6 mg. The observed weight losses calculated from a known tare weight, ranged between 92–94 mg, which is within experimental error. The shape of these curves (in the isothermal region) is sigmoidal with an extended linear region during the central portion (about 50 mg) of the reaction. Reaction rates for the linear region were obtained directly from the recordings, in terms of mg/min per 400 mg sample.

An atmosphere of flowing helium was used to carry away the gaseous decomposition products, SO$_2$, SO$_3$ and O$_2$. It was first determined that a flow-rate of 3 l/min was required to insure freedom from flow-rate effects. This was done by using flow-rates of 1, 2, 3 and 4 l/min at 684°. The respective reaction rates observed were 5.82, 7.98, 8.42 and 8.44 mg/min per 400 mg sample.

Six isothermal decompositions were carried out at temperatures ranging between 639–721°. The measured reaction rates are tabulated in Table 2. An Arrhenius plot of these data, using least squares treatment, gives a value of 58.6 ± 0.6 kcal/mole (one sigma limits) for the activation energy.

The probable rate limiting mechanism for the decomposition may be deduced from the shape of the weight vs. time curves. The sigmoidal curves observed with a central linear region, may be obtained by assuming that nucleation and growth occur at comparable rates. A quantitative treatment of surface nucleation and growth was developed by JOHNSON and MEHL[13] for grain boundary nucleation in metallurgical transformations. Their treatment has been successfully applied to the kinetics of a gas-solid reaction by ARONSON *et al*⁽¹⁴⁾ Because the equations are algebraically complex, JOHNSON and MEHL plotted a series of curves which could be compared with experimental data

---

[9] K. J. NOTZ and H. H. JAFFE, *J. Amer. Ceramic Soc.* **43**, 53 (1960).

[10] I. W. DEWING and F. D. RICHARDSON, *Trans. Faraday Soc.* **55**, 611 (1959).

[11] R. M. GRUVER, *J. Amer. Ceramic Soc.* **34**, 353 (1951).

[12] F. C. KRACEK, *Smithsonian Physical Tables* (9th Rev. Ed.) Tables 124, pp. 126–129 (1954).

[13] W. A. JOHNSON and R. F. MEHL, *Trans. Am. Inst. Mining and Met. Engng.* **135**, 416 (1939).

A complete comparison of the uranyl sulphate decomposition curves with the JOHNSON and MEHL curves is not possible since the first part of the decomposition curves is missing due to the time lag before isothermal control is attained However, a comparison with that part of the curve which is valid shows good agreement with those curves which have a λ of 1·25, corresponding to 11–80 nuclei per particle The extended linear portions of the curves are due to a constant active surface area at which reaction is occurring Since the surface area of the starting UO_2SO_4 was 0 81 m^2/g, the area of the active surface during the period of constant rate is estimated as 0 6 m^2/g Thus the rate data given in Table 2 in terms of a 400 mg sample could more aptly be stated in terms of an active area of approximately 0 25 m^2, since active area is the basic parameter

The initial, accelerating portion of the reaction represents a period of nucleation rate control when only part of the total uranyl sulphate surface has become active The final, decelerating part of the decomposition is caused by growth rate control, since all the surface is active, but the total surface is decreasing

Surface areas obtained on the U_3O_8 products at 655 and 721° provide supporting data for the nucleation and growth rate model, particularly so since the volume change factor on decomposition also favours a non-diffusion limited rate model In studying metal oxidation, PILLING and BEDWORTH⁽¹⁵⁾ found that a protective film of metal oxide was formed only if the molar volume ratio of product oxide to base metal was in the range 0 8–1 4 This of course would cause the oxidation rate to be diffusion limited In the present case, the molar volume ratio of $\frac{1}{3}U_3O_8$ (density = 8 33 g/cm^3) to UO_2SO_4 (density = 4 88 g/cm^3) is 0 45, small enough to postulate physical disruption of the U_3O_8 layer This was verified by the surface areas obtained for two U_3O_8 decomposition products 8 7 m^2/g (reacted at 655°) and 7 2 m^2/g (reacted at 721°) In fact, the large increase in surface area (UO_2SO_4 was 0 81 m^2/g) shows that extensive disruption of the particles actually occurred Thus diffusion of the decomposition gases away from the reaction sites would not be a rate limiting factor The lower U_3O_8 surface area obtained at the higher temperature is due to sintering of the U_3O_8 which is known to occur above 600°

The rate law for the decomposition of UO_2SO_4 may be expressed as

$$\text{Rate (mg/min)} = zS \exp(-E/RT)$$

for decomposition in an inert atmosphere The activation energy has been determined as 58 6 kcal/mole The active surface, S, has been shown to be a function of time or degree of reaction In the present case, it was estimated as 0 25 m^2 during the linear portion of the reaction It is also a function of particle size, since the relative importance of nucleation rate decreases as particle size increases For the extreme case where surface nucleation is complete before over-all conversion is very far advanced (i e , very large particles), decomposition will follow the phase-boundary rate law On the other extreme, where conversion of a particle is complete shortly after nucleation

---

(14) S ARONSON, R B ROOF, JR and J BELLE, *J Chem Phys* **27**, 137 (1957)

(15) N B PILLING and R E BEDWORTH, *J Inst Metals* **29**, 552 (1923)

(i e, very small particles), a first-order rate will be observed In either case, the above rate expression is still valid since it refers only to active, i e, nucleated surface Evaluation of the proportionality constant, z, leads to

$$\text{Rate} = 11 \times 10^{11} \exp(-58{,}600/RT)$$

where the rate is given in mg of weight lost per minute per square metre of active surface

Acknowledgement—The authors are thankful to the National Lead Company of Ohio for their generous cooperation

J. Inorg. Nucl. Chem. 1963, Vol. 25, pp. 859 to 865. Pergamon Press Ltd. Printed in Northern Ireland

THE REACTION OF SILVER OXIDES WITH POTASSIUM HYDROXIDE

T. P. Dirkse, L. A. Vander Lugt and H. Schnyders
Department of Chemistry, Calvin College, Grand Rapids 6, Michigan

(*Received* 3 *January* 1963)

Abstract—The dissolution of silver oxides in aqueous potassium hydroxide solutions has been followed by determining solubility and by observing the changes in potential of a silver electrode in such solutions. The effect of solubility with time has been studied and the identity of the black decomposition product has been determined. The extent to which silver oxides dissolve in aqueous potassium hydroxide is determined by several reactions.

This problem arises in the observation that Ag_2O and AgO have approximately equal solubilities in KOH solutions at 25°C.[1] This seems to violate a general rule that two compounds having a given element in common and in different oxidation states have different solubilities. The similarity in solubilities suggests that perhaps the same solute species exists in both cases.

Amlie and Rüetschi[2] attacked this problem by measuring the diffusion currents at a rotating Pt electrode in solutions prepared by dissolving Ag_2O and AgO in aqueous KOH. The same diffusion currents were obtained in each case showing that the same ionic species is present regardless of which oxide of silver is dissolved in the KOH solutions. These investigators suggested that the AgO decomposes to a form of the monovalent silver. They determined the rate of this decomposition of AgO in KOH solutions by measurement of oxygen evolution. Pleskov[3] using rotating Au and Pt electrodes, also showed that the divalent silver ions are unstable in alkaline solutions.

Several questions still remain, however. Such questions are: (1) is AgO soluble at all in alkaline solutions? (2) does AgO dissolve and then decompose in solution to form an ion containing Ag in the oxidation state of one? (3) is the ion containing monovalent silver stable in KOH solutions? The purpose of this work was to attempt to cast some light on these questions.

EXPERIMENTAL

Two kinds of measurements were made: (a) the solubility of Ag_2O and AgO in KOH solutions and (b) the change in potential of a Ag electrode dipped into a 1 N KOH solution in which silver oxides were being dissolved. This was done at 5° and at 27°C.

The solubilities of the silver oxides were measured by treating the KOH solutions with excess oxide, filtering the solutions through a fine Pyrex glass frit and titrating the filtered solutions potentiometrically with KI to determine silver content.[1, 4] Commercially available silver oxides were used. The solubilities were determined about an hour after the oxide was added and also over a period of months.

The potential of the Ag wire electrode was measured against a HgO/Hg reference electrode with

---

[1] T. P. Dirkse and B. Wiers, *J. Electrochem. Soc.* **106**, 284 (1954).

[2] R. F. Amlie and P. Rüetschi, *J. Electrochem. Soc.* **108**, 813 (1961).

[3] Yu. V. Pleskov, *Dokl. Akad. Nauk. S.S.S.R.* **117**, 645 (1957).

[4] H. L. Johnston, F. Cuta, A. B. Garrett, *J. Amer. Chem. Soc.* **55**, 2311 (1933).

1 N KOH being used throughout The KOH solution was stirred magnetically while a constant stream of N_2 passed over the surface of it The voltage of this cell was measured by a General Radio Model 1230A DC Electrometer using an input impedance of $10^9\ \Omega$ This electrometer also supplied a signal to an L & N Model H recorder which gave a continuous record of the voltage changes in the cell The voltage was recorded for about an hour before and after the addition of the silver oxides After the run the solution was filtered through a fritted (fine) glass crucible and then analysed for dissolved silver as described above

RESULTS

The results of the voltage measurements are shown on Fig 1 Only that part of the record is given which shows the effect of adding silver oxides to the KOH solution The values for the molarity of the silver given in each panel is that determined immediately after the run was terminated

The voltage of the cell rises immediately after the oxides have been added and soon levels off, approaching a value of approximately 250 mV for the cell The same limiting value is approached at both temperatures and for both Ag_2O and AgO It is the same value obtained by HAMER and CRAIG(6) for the cell

$$\mathrm{Hg, HgO} \mid \mathrm{NaOH\ (aq)} \mid \mathrm{Ag_2O, Ag}$$

In order to interpret these results it is first of all necessary to know whether the voltage is determined by the nature and concentration of the solute species and/or by the nature of the silver electrode To clarify this point the potential of a clean Ag wire electrode was measured against a HgO/Hg reference electrode in three different solutions These solutions were all 1 N KOH To the first Ag_2O had been added and the Ag concentration was 9×10^{-5} M To the second AgO had been added and the Ag concentration was also 9×10^{-5} M Both of these solutions were unsaturated with respect to Ag_2O at room temperature The third solution was plain KOH The measured voltage was approximately the same in each case (about 240 mV) and decreased gradually over a period of 16 hr to about 160 mV The fact that the Ag electrode behaved similarly in each case shows that the potential of the Ag wire was not determined by the dissolved silver species in these solutions Further evidence of this lies in the fact that the voltages shown in Fig 1 rise, first rapidly, then slowly, as soon as the oxide is added, but do not go through a maximum as the solubility values do Although aqueous KOH solutions of both Ag_2O and AgO contain, at least to some extent, the same solute species,(2) these species are not, in this experiment, potential determining for the silver electrode

It appears then that the voltages given in Fig 1 are for the Ag_2O/Ag electrode and not for a metal–ion electrode, e g , $Ag(OH)_2^-/Ag$ This is so even though the type and concentration of dissolved silver-containing ion is the same whether AgO or Ag_2O is added to the KOH solution In fact, the formation of the Ag_2O/Ag electrode is undoubtedly related to this phenomenon Apparently Ag_2O is deposited on the Ag electrode to give an Ag_2O/Ag electrode, and thus the voltage reported by HAMER and CRAIG

This is more readily explained when note is taken of the results of solubility determinations, Table 1 In each case the silver oxide solubility goes through a maximum and then decreases, the concentration after a week being less than after an hour Although the results in Table 1 give solubilities only after 1 hr and after one week, other measurements have shown that the decrease in solubility is noted within a few hours(1, 6) The best interpretation seems to be that the dissolution process is due to a reaction of the oxides with the KOH After an induction period other processes

---

(6) W J HAMER and D N CRAIG, *J Electrochem Soc* **104**, 206 (1957)

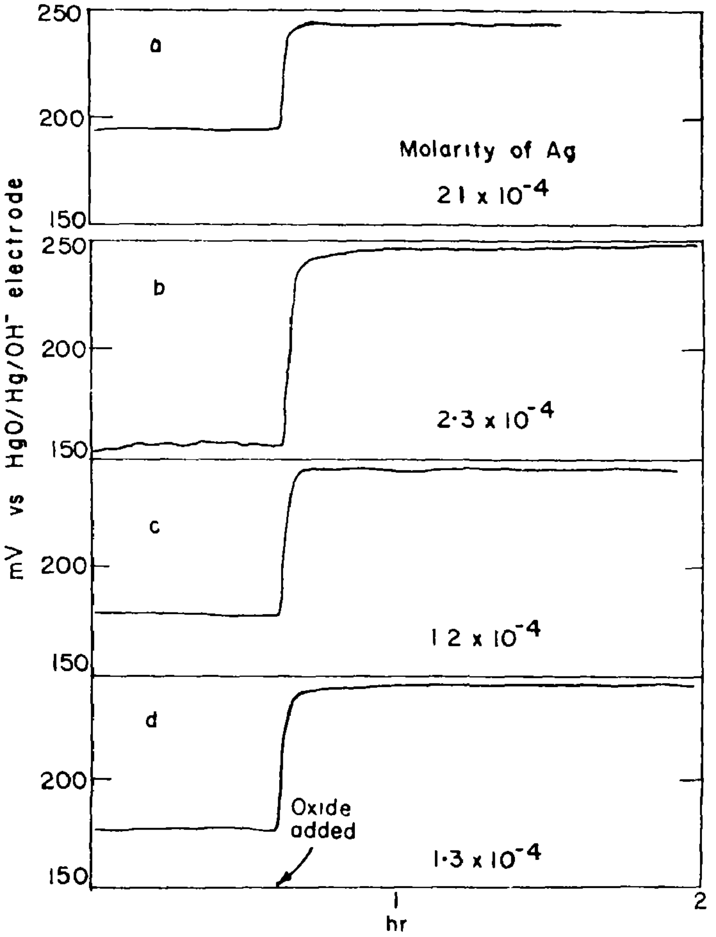


FIG. 1 - Change in potential of Ag wire immersed in 1 N KOH (a) Ag_2O added at 27 C, (b) AgO added at 27°C, (c) Ag_2O added at 5°C, (d) AgO added at 5 C

TABLE I —CONCENTRATION OF SILVER OXIDES IN 1 N KOH (× 10^4)

	Ag_2O		AgO	
Temp	After 1 hr	After 1 week	After 1 hr	After 1 week
5 C	1·19	0·9	1·3	0·88
27°C	2·17	1·7	2·48	1·72

---

(6) H P GREGOR, N NAKAJIMA, D H GOLD E M LOEBL, G K HOESCHELE, R DOGAN *A Study of the application of Ion Exchange to Electric Batteries*, Report of 31 August 1954 on Contract No NObs-62383, Polytechnic Institute of Brooklyn, Brooklyn, N Y

may take place which tend to reduce the solubility giving rise, after a time lag, to an apparent equilibrium concentration Equations (1) and (2) represent possible processes for Ag_2O

$$Ag_2O + H_2O + 2OH^- \quad 2Ag(OH)_2 \tag{1}$$

$$2Ag(OH)_2 \quad Ag_2O + H_2O + 2OH^- \tag{2}$$

The Ag_2O from reaction (2) may deposit on the Ag wire thus producing the Ag_2O/Ag electrode The decrease in solubility is also due to reaction (9), to be discussed later

With AgO the solubility reaches a higher maximum than with Ag_2O, Table I Equations (3) and (4) and (2) represent the possible reactions here

$$AgO + H_2O + OH \quad Ag(OH)_3 \tag{3}$$

$$2Ag(OH)_3 \quad 2Ag(OH)_2 + H_2O + \tfrac{1}{2}O_2 \tag{4}$$

On Fig 1 the time lapse before the voltage begins to level off is roughly the same in all cases noted there, about 3 to 4 minutes This suggests that the same process could be responsible for this change in each instance This would be reaction (2) If this is so then reaction (4) would appear to be rapid in comparison Yet AMLIE and RUETSCHI⁽²⁾ found this to be a relatively slow reaction If the reactions postulated thus far are correct then they were making measurements on reaction (4) It is likely, however, that in our experiments the Ag electrode served to catalyse reaction (4) Another possibility is that the silver electrode reacts directly with the AgO as follows

$$AgO + Ag = Ag_2O$$

$$\text{or} \quad Ag(OH)_3 + Ag \quad Ag_2O + H_2O + OH$$

This reaction has been noted earlier ⁽¹ ²⁾

In any event, the Ag electrode is undoubtedly involved, directly or indirectly, in reaction with the silver oxides and this may give rise to phenomena that do not occur when no electrode, Ag or any other, is present For this reason, evidence based on solubilities is considered to be more trustworthy

Such measurements show that the peak solubility is greater when AgO is added than when Ag_2O is added to the KOH solution This indicates that AgO is soluble in the KOH solutions and that its solubility is greater than that of Ag_2O, in accord with the general rule for the relative solubilities of oxides of a given metal in different valence states This is followed by other processes which reduce the amount of dissolved material Reaction (4) is one such process,⁽²⁾ and thus the solubilities of the two oxides, Ag_2O and AgO, appear to be the same in KOH solutions after equilibrium has been reached This is true at 5 C as well as at room temperature

The fact that the solubility of the silver oxides in 1 N KOH solutions varies with time suggested a more extensive study of this time factor Samples of Ag_2O and AgO were added to 1 N KOH solutions Half of these were kept where they would be exposed to daylight and the others were kept in the dark Samples were removed, filtered as before and analysed for dissolved silver content In some cases a solution was filtered and then allowed to stand for some time It was then filtered again before analysis All this was done at room temperature, about 22°C

The results of this work are shown on Fig 2 The solutions in which an excess of undissolved oxide was always present show about the same solubility, with the exception of the solution containing excess Ag_2O and exposed to daylight Here the solubility gradually decreased with time For the other solutions there was little variation with time

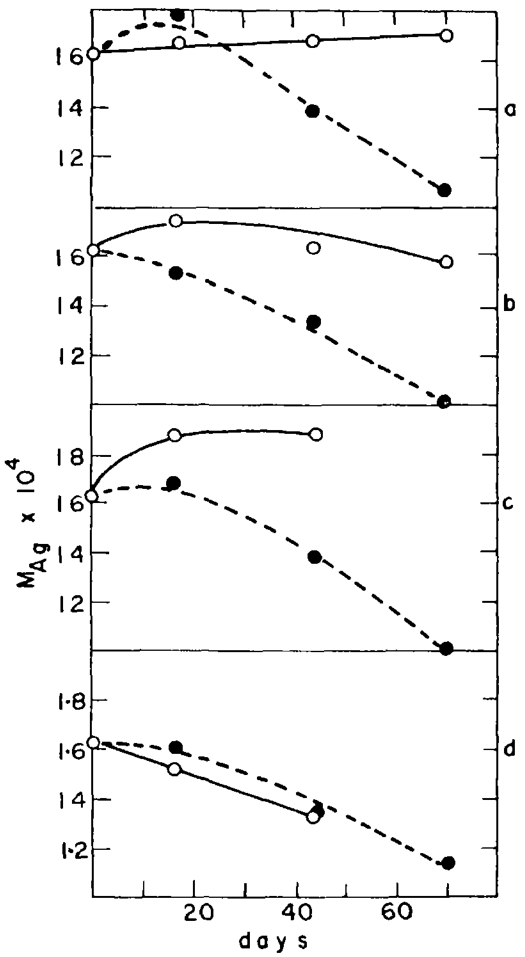


Fig 2 Variation of solubility of silver oxides in 1 N KOH with time open circles, excess undissolved oxide present, closed circles, no excess undissolved oxide present panel (a) AgO, mixture kept in the dark, panel (b) AgO, mixture exposed to daylight panel (c) Ag_2O, mixture kept in the dark, panel (d) Ag_2O mixture exposed to daylight

The fact that the results in Fig 2 show a somewhat different trend than those in Table I can be accounted for by the difference in stirring procedure For the results reported in Table I the mixtures were stirred continuously throughout the entire run For the mixtures reported in Fig 2, however, the stirring was not continuous Here the solutions were shaken by hand each day This undoubtedly prevented complete equilibrium from being attained during the first few hours This is especially true when as noted below, reactions are taking place constantly in these solutions

Filtered solutions, i e , apparently saturated solutions which were allowed to stand without an excess of undissolved oxide present, showed gradual decrease in solubility over a period of time. This was true of all solutions and seemed to be independent of photo effects. This agrees with observations made during this series of runs as well as in other but similar situations. The observation is that filtered solutions of silver oxides in aqueous KOH gradually form a finely divided black deposit. If this is filtered off and the solution allowed to stand, more black deposit will be formed in time.

Samples of the black deposit were collected from solutions of Ag_2O in 7 N KOH and subjected to X-ray analysis. The only lines obtained in the diffraction pattern were those of metallic silver. The three most intense lines of the silver X-ray diffraction pattern were present in each case. Thus the formation of the fine black deposit is a result of further interaction of the silver species with the electrolyte to form metallic silver. This silver could be formed by the reduction of the oxide as follows

$$Ag_2O + H_2O + 2e = 2Ag + 2OH^- \qquad E^\circ = +0.34\ V \tag{5}$$

and

$$2OH^- - 2e = \tfrac{1}{2}O_2 + H_2O \qquad E^\circ = -0.40\ V \tag{6}$$

This reaction, however, is not a spontaneous reaction and hence it is unlikely that this is the means by which the black deposit is formed. The metallic silver may also be formed by reduction of the dissolved silver-containing ion

$$2Ag(OH)_2^- + 2e = 2Ag + 4OH^- \qquad E^\circ = +0.78\ V \tag{7}$$

and

$$2OH^- - 2e = \tfrac{1}{2}O_2 + H_2O \qquad E^\circ = -0.40\ V \tag{8}$$

E° for reaction (7) has been calculated using the free energy of formation of $Ag(OH)_2^-$.⁽¹⁾ The reduction of $Ag(OH)_2^-$ to Ag is thermodynamically spontaneous by the above mechanism.

It is known that the dissolved silver-containing ion is the same whether AgO or Ag_2O has been dissolved in the KOH.⁽²⁾ The nature of this ion has not, however been resolved completely. The data of Johnston, *et al.*,⁽⁴⁾ on the solubility of Ag_2O in somewhat dilute alkaline solutions indicates AgO^- or $Ag(OH)_2^-$. Pleskov and Kabanov⁽⁷⁾ used more concentrated solutions of KOH for determining the solubility of Ag_2O and concluded that the species is $Ag_4O(OH)_2$. Attempts by others to verify this work led to the conclusion that no polynuclear argentate is formed but rather $Ag(OH)_2^-$.⁽⁸⁾

Assuming that the dissolved species is $Ag(OH)_2^-$ it appears then that this undergoes a slow reaction with the electrolyte giving an over-all reaction as follows

$$2Ag(OH)_2^- = 2Ag + \tfrac{1}{2}O_2 + H_2O + 2OH^- \tag{9}$$

This can account for the continued decrease of dissolved silver species in filtered KOH solutions that are supposedly saturated with silver oxides. This black deposit of Ag has been observed especially on the inside of polyethylene bottles in which such solutions have been stored. This reaction proceeds continually and only when excess undissolved oxides are present does the dissolved silver content remain constant, because then some of the undissolved oxide can replace that lost by reaction (9)

---

(7) Yu. V. Pleskov and B. N. Kabanov, *Zh. Neorg. Khim.* **2**, 1807 (1957).

(8) P. J. Antikainen, S. Hietanen, L. G. Sillen, U.S. Dept. Comm., Office of Tech. Serv., PB Report 145,613, 11 pp. (1959).

The solubility, then, of the silver oxides in KOH solutions is the net result of several reactions, e g , reactions (1) (4), (7) and (8) The values for silver content obtained on analysis will be determined by the relative extents to which these various reactions have taken place Further studies of the factors which affect the rate of reaction (9) are in progress

Acknowledgements—The authors wish to express their thanks and appreciation to the Office of Naval Research for a grant in support of this work, and to the M Ames Chemical Works, Inc for supplying the oxides

J. Inorg. Nucl. Chem. 1963. Vol. 25, pp. 867 to 874. Pergamon Press Ltd. Printed in Northern Ireland

THE ANION EXCHANGE OF METAL COMPLEXES—XII(1)

THE CADMIUM AND MERCURY—HALIDE SYSTEMS

Y. Marcus and I. Eliezer
Radiochemistry Department, Israel Atomic Energy Commission,
Soreq Research Establishment, Rehovoth, Israel

(*Received* 20 *November* 1962)

Abstract—The distribution of trace cadmium and mercury ions between Dowex-1 strong base anion exchanger, and solutions of hydrochloric acid, lithium chloride and bromide and sodium chloride, bromide and iodide has been measured. Resin ligand activity functions for these electrolyte–resin systems were obtained and used to show that the predominant complex species in both solution and resin, over the halide concentration range one M to saturation, is the tetrahalide. Only in hydrochloric acid (but not in hydrobromic acid) is there evidence for other species, which may be the undissociated acids, as suggested in the literature. The results for the other electrolytes indicate the validity of the effective ligand activity concept also in bromide and iodide solutions.

As already often pointed out(2, 3), anion exchange separations of metal ions have been mainly confined to chloride solutions, and little effort has been spent on investigating solutions of the heavier halides. In some cases, it has shown(3) that better separations are possible in bromide than in chloride solutions. In order to apply the anion exchange method of studying metal complex formation(4) to bromide and iodide solutions, information on the ligand activity in the resin is required. This may be done conveniently by measuring the distribution of a stable anion.(4, 5) It should also be profitable to test the applicability of the concept of an effective ligand activity a $m\gamma$, discussed fully for chloride as ligand,(5) also to bromide and iodide solutions.

While the cadmium chloride system has already been studied in detail,(6) the information on the bromide and iodide systems is very scant. A number of workers noted the strong absorption of cadmium from iodide solutions(7–10) and a few distribution data were given by Fronaeus(8) for these and for bromide solutions. A preliminary evaluation of the latter data(4) showed fair agreement with published complex formation constants. The absorption of mercury from hydrochloric and hydrobromic acids has been measured,(3, 11) but the very small scale diagrams in which the data have been presented precludes quantitative evaluation More useful distribution data have recently been published by MIZUMACHI(12) for solutions of hydrochloric acid, lithium chloride and mixtures of the two

---

(1) Previous paper in series: I. Eliezer and Y. Marcus (XI. Application of the constant ionic medium method to the mercury halide system.) *J. Inorg. Nucl. Chem.* In Press.

(2) K. A. Kraus and F. Nelson *A.S.T.M. Spec. Tech. Publ.* No. 195 (1958).

(3) T. Anderson and A. Bye Knutsen *Acta Chem. Scand.* **16**, 849 (1962).

(4) Y. Marcus and C. D. Coryell, *Bull. Res. Counc. Israel* **8** A, 1 (1959). (Part I).

(5) Y. Marcus and D. Maydan, *J. Phys. Chem.* In press (Part VIII).

(6) Y. Marcus, *J. Phys. Chem.* **63**, 1000 (1959), (Part III).

(7) I. Leden, *Svensk Kem. Tidsr.* **64**, 145 (1952).

(8) S. Fronaeus, *Svensk Kem. Tidsr.* **65**, 1 (1953).

(9) R. E. Baggott and R. G. W. Willcocks *Analyst* **80**, 53 (1955).

(10) S. Kallmann, H. Oberthin and R. Liu *Analyt. Chem.* **30**, 1846 (1859).

(11) K. A. Kraus and F. Nelson, *Proceedings of the International Conference on the Peaceful Uses Atomic Energy, Geneva* 1955, 7, p. 113 United Nations, (1956).

The present work concerns the distribution of mercury and cadmium tracers between Dowex-1 strongly basic anion exchanger in the appropriate halide form and solutions of hydrochloric acid, lithium chloride and bromide, and sodium chloride, bromide and iodide The distribution of iodide and perrhenate tracers between the resin and sodium bromide and iodide solutions respectively, has also been measured In conjunction with previously published data for zinc chloride(5) and bromide,(3, 13) and cadmium chloride(6) the anion exchange behaviour of the three II B group elements zinc, cadmium and mercury is compared for the three halides

EXPERIMENTAL

Materials The following radioactive tracers were used ^{203}Hg, obtained from Oak Ridge National Laboratory in nitrate solution, ^{115}Cd (54 hr) as oxide and ^{186}Re (91 hr) as ammonium perrhenate, obtained from Israel Research Reactor, and ^{131}I, obtained carrier-free from the Commissariat de l'Energie Atomique All tracers were used at 10^{-1}–10^{-6} M, so that resin loading was usually less than 1 per cent and always less than 3 per cent The resin was Dowex-1 × 10, A G from Bio Rad, and all other chemicals were of analytical reagent grade The resin was treated and converted into the appropriate halide form as described before(1) No distribution measurements were made with hydrobromic acid and hydroiodic acid solutions because of rapid oxidation on contact with the resin, and of the strong interaction of bromine and iodine with the resin

Methods Distribution measurements were made by batch equilibrations, as described previously(1) The continuous circulation method( ) could not be used for bromide and iodide solutions because of a too slow rate of equilibration, already predicted by KRAUS and NELSON(2)

RESULTS

The invasion of the resin has already been measured for hydrochloric acid,(14, 15) lithium chloride,(15, 1, 5) sodium chloride,(5, 15) and lithium bromide,(3) but no data were available for sodium bromide and iodide Using a stable anion B such as iodide or perrhenate, should, according to MARCUS and CORYELL,(4) yield values for F_B, the invasion function, where for univalent ions*

$$F_B = \log D_B + \log a \qquad (1)$$

For sodium bromide solutions iodide tracer was used, whereas perrhenate was used for sodium iodide solutions The results are shown in Fig 1 Values for the activity coefficients of sodium bromide and iodide, required for calculating a, were obtained from ROBINSON and STOKES,(16) except for high concentrations of sodium iodide, where data of MILLER and SHERIDAN(17) were used No data were available for high concentrations of sodium bromide and extrapolation of data from below 4 m,(16) following the curve for the similar salt sodium thiocyanate,(17) was resorted to. The values obtained agreed with preliminary data obtained in this laboratory.(18)

---

* MARCUS and CORYELL(4) defined ${}_r\Gamma_a = \log D_B + \log a - \log D_B$ (at $a = 1$) which differs from definition (1) by a constant ($\log D$ at $a = 1$), while MARCUS and MAYDAN(5) use the resin ligand effective activity $\bar{a}$, where $\log \bar{a} = {}_r\Gamma_a + \log \bar{a}$ (at $a = 1$), i e $\log a$ also differs from F_B by a constant

(12) K MIZUMACHI, *J Chem Soc Japan, Pure Chem Sect* **83**, 61 (1962)

(13) R H HERBER and J W IRVINE, JR *J Amer Chem Soc* **76**, 987 (1954)

(14) K A KRAUS and G E MOORE, *J Amer Chem Soc* **75**, 1457 (1953)

(15) F NELSON and K A KRAUS, *J Amer Chem Soc* **80**, 4154 (1958)

(16) R A ROBINSON and R H STOKES, *Electrolyte Solutions* Butterworth, London (1955)

(17) M L MILLER and C L SHERIDAN, *J Phys Chem* **60**, 184 (1956)

The functions F_I for sodium bromide and F_{ReO_4} for sodium iodide were calculated by Equation (1), and are also shown in Fig. 1, as well as ${}_rF_a$ for lithium bromide,(3)

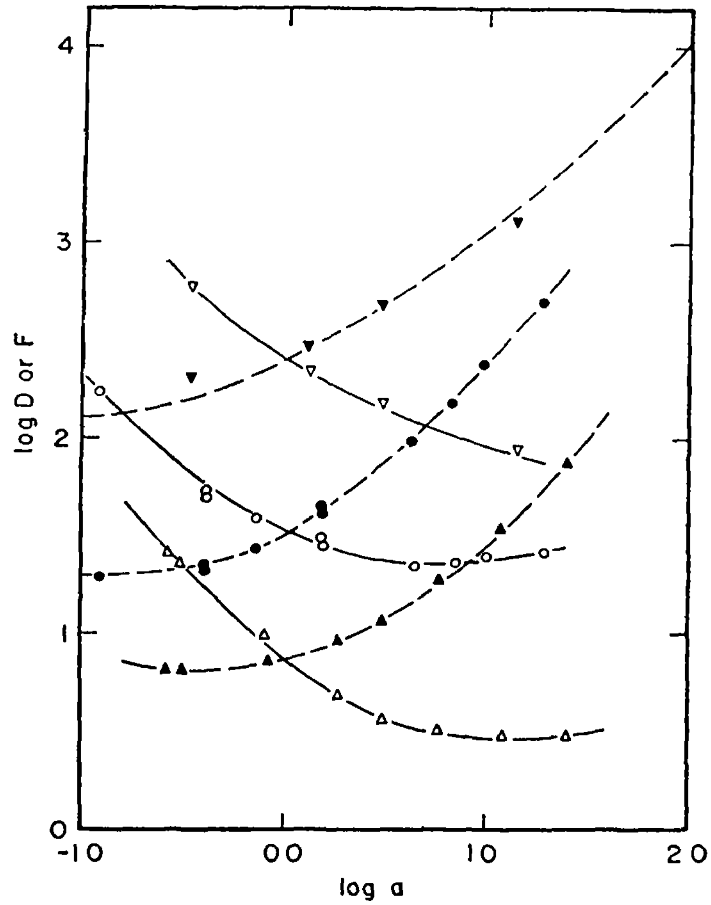


Fig. 1. Distribution coefficients (log D) and invasion functions (F = log D − log a) of stable anions vs effective ligand activities (log a). ▽ ReO_4^- in LiBr (data from Chu(19)), ○ I^- in NaBr, △ ReO_4^- in NaI, empty symbols D, full symbols F. — smoothed F values, by interpolation, except for LiBr where the curve from Anderson and Knutsen(3) was used, displaced by 2.40 upwards.

displaced upwards by 2.40, which agrees fairly well with values calculated from the data given by Chu(19) for perrhenate.

The distribution coefficients for tracer mercury and chloride solutions are shown in Fig. 2. The data given by Mizumachi(12) for hydrochloric acid and lithium chloride are in good agreement with the present data, as are the rough curves of Kraus's(11) and

(18) J. Penciner and Y. Marcus, Unpublished work.

(19) B. Chu, Ph.D. Thesis, Cornell University (1959).

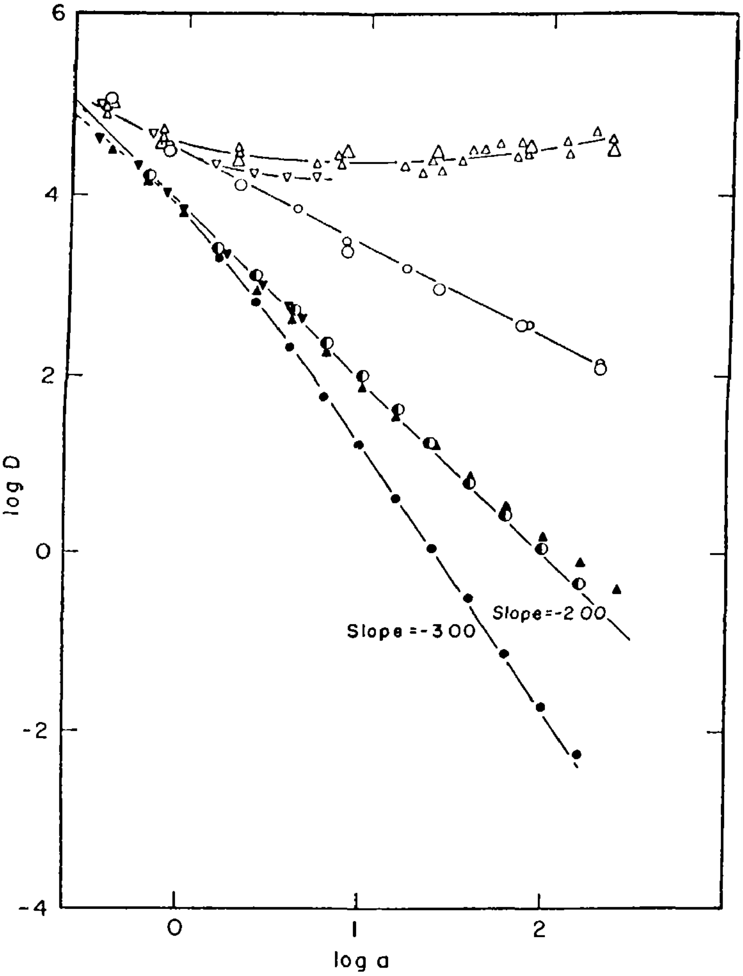


FIG. 2.—Distribution coefficients (log D) of mercury ions vs. effective ligand activities (log a): ○ HCl, ◐ HCl(12), △ LiCl, LiCl(12), ▽ NaCl; ●, ▲, ▼ log D_{Hg} − 2 log $\bar{a}$ for HCl, LiCl and NaCl resp.; ◑ log D_{Hg} − log $\bar{a}$ for HCl.

of ANDERSON(3) (not shown). According to MARCUS and CORYELL,(4) the distribution coefficient for a tracer metal M^{2+} is given by

$$\log D_M = \log K_M + pF - \log \sum_{2}^{N} \beta_i^{*} a_i \qquad (2)$$

where K_M is a constant independent of a, p is the charge of the anionic resin complex, F is the invasion function (F_B, ${}_rF_a$ or $\bar{a}$), β_i^{*} is the stability constant, referred to the neutral complex, for the complex with charge i, and N the coordination number.

The stability of the mercury halide complexes is such(20) that above 1M halide X, only MX_4^{2-} need be taken into account. From (1) and (2),

$$\log D_M - pF = \log K_M' - 2 \log a \qquad (3)$$

where K_M' is a constant, depending on the definition of F (whether as F_B, ${}_rF_a$ or $\bar{a}$).

The correct value of p has been selected if a plot of log $D_M - pF$ vs. log a gives straight line of slope −2.00 required by the charge of the complex in the aqueous phase. Using a value of $p = 2$, and appropriate[(5)] I values, such a line was indeed obtained for lithium and sodium chloride solutions, Fig. 2, while for hydrochloric acid the slope at high concentrations was −3.00. This hydrogen ion effect will be dealt with separately below.

---

(20) Y. MARCUS, *Acta Chem. Scand.* **11**, 599 (1959).

At the lowest chloride concentrations, the data $\log D_M - 2\Gamma$ show a slight deviation, which is due to incomplete formation of $HgCl_4^{2-}$ in the aqueous phase. Using the value $\log k_4 = 1.05$[(20)] for the equilibrium constant for conversion of $HgCl_3^-$ to $HgCl_4^{2-}$, completely accounts for this discrepancy.

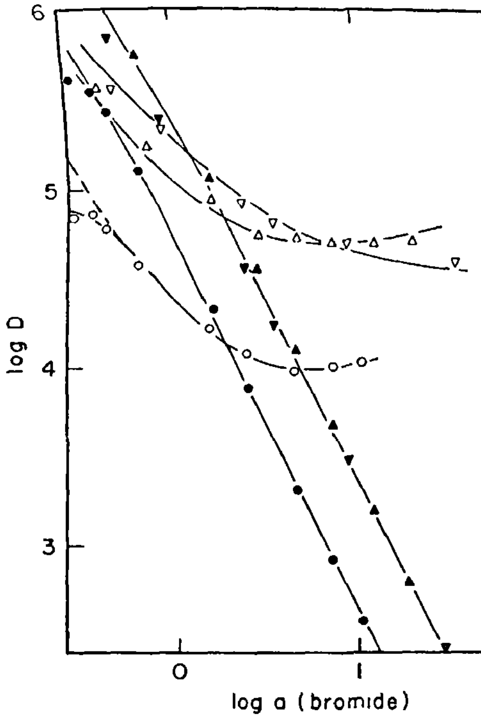


FIG. 3.—Distribution coefficients ($\log D$) of mercury and cadmium in bromide solutions vs. effective ligand activities ($\log a$). △ Hg in NaBr, ▽ Hg in LiBr, ○ Cd in NaBr. ▲, ▼, ● $\log D - 2F$ for respective systems, straight lines have slope −2.00, curves are calculated.

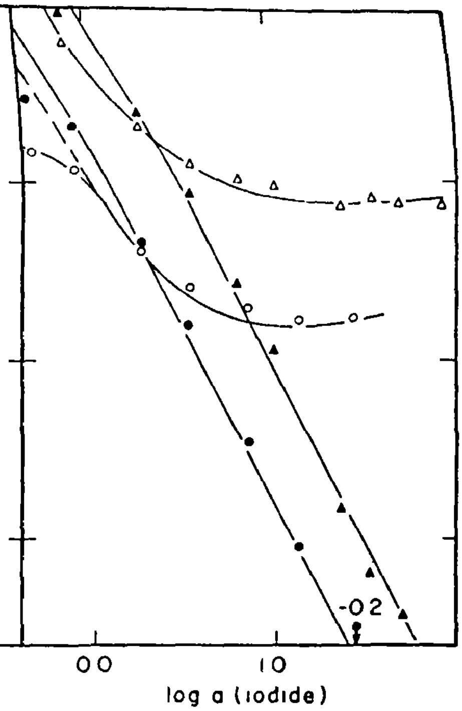


FIG. 4.—Distribution coefficients ($\log D$) for mercury and cadmium in iodide solutions vs. effective ligand activities ($\log a$). △ Hg in NaI, ○ Cd in NaI. ▲, ● $\log D - 2F$ for respective systems, straight lines have slope −2.00, curves are calculated.

The results for mercury and cadmium tracers and bromide and iodide solutions are shown in Figs. 3 and 4. For concentrations above 1M for cadmium and all concentrations measured for mercury, Equation (3) applies, with $p = 2$, using I_I and I_{ReO_4} from Fig. 1, for bromide and iodide solutions respectively. The deviations for cadmium below 1M are explicable by incomplete formation of $CdBr_4^{2-}$ and CdI_4^{2-} in the aqueous phase, and published formation constants can be used to correct for the deviations. The experimental results at the high distribution coefficients involved, are, however, insufficiently accurate for an independent estimation of the formation constants. This might probably be accomplished using resins with lower crosslinking, which should considerably decrease the distribution coefficients for resin complexes with $p = 2$.[21]

DISCUSSION

The principal conclusion from the above results is that the effective ligand activity a adequately describes the required quantities in the mass action law expressions at high concentrations. This has now been demonstrated for various alkali (lithium, sodium, potassium, ammonium, cesium) halide (chloride, bromide, iodide) solutions with a variety of tracer anions, with as different structures as iodide, perrhenate, tetrachlorozincate or halomercuriate, both in the present work as in others.[3–5] This is encouraging for workers interested in studying formation of weak complexes, requiring high ligand concentrations.

Another point to be noted is that mercury (II) halides may be used in halide solutions (except hydrochloric acid) to determine the invasion function F, in the same way as anions such as iodide or perrhenate. The failure of the measurements in hydrochloric acid to conform to expectation (Fig. 2), however, warrants discussion. It is interesting, in this context, to compare results in hydrochloric and hydrobromic acid where, unfortunately, only the rough data of ANDERSON and KNUTSEN[3] are available. Combining Equations (1) and (3) yields for $p = 2$

$$\log D_{Hg} - 2 \log D_{Re} = \text{const} \tag{4}$$

This equation is obeyed by mercury in hydrobromic acid, as seen in Table 1 and in alkali halide solutions as shown above, but not in hydrochloric acid, where, instead, the relationship $\log D_{Hg} - \log D_{Re} = \text{const}$ is obeyed.

TABLE 1. ANION EXCHANGE DISTRIBUTION OF MERCURY (II), CORRECTED FOR INVASION, FOR HYDROCHLORIC AND HYDROBROMIC ACIDS

	HCl		HBr	
Molarity	$\log D_{Hg} - \log D_{Re}$	$\log D_{Hg} - 2 \log D_{Re}$	$\log D_{Hg} - \log D_{Re}$	$\log D_{Hg} - 2 \log D_{Re}$
0.5	1.1	2.4	2.7	0.4
1.0	1.3	2.7	2.6	0.4
2.0	1.4	1.2	2.3	0.3
3.0	1.5	0.7	2.2	0.4
4.0	1.4	0.6	2.1	0.5
5.0	1.3	0.5	2.0	0.5
6.0	1.2	0.5	1.8	0.4
7.0	1.2	0.3	1.7	0.4
8.0	1.2	0.1		

A more detailed examination shows that Equation (3) is obeyed by using $p = 1$ for hydrochloric acid, as the slope $\partial(\log D - F)/\partial \log a$ has the required value of 2.00 (Fig. 2, half-filled points). This means that whereas in the aqueous phase the predominant species is $HgCl_4^{2-}$ as in lithium or sodium chloride solutions, in the resin a mononegative complex predominates. This is unlikely to be $HgCl_3^-$, since this does not explain the "hydrogen ion effect", but it could possibly be $HHgCl_4^-$. The same species has been used by MIZUMACHI[12] to explain his results on the absorption of tracer mercury (II) on an anion exchanger from mixed hydrochloric acid lithium chloride solutions The preferential association of hydrogen ions with the tetrachloromercurate ions in the resin phase, compared with the aqueous solutions, may be explained in terms of the low effective dielectric constant in the former [21] Solid chloromercuric acids are well known [22] The non-formation of $HHgBr_4^-$ in the resin is presumably due to the greater strength of this acid, analogous with the greater strength of HBr compared with HCl

---

[21] Y. MARCUS and D. MAYDAN, *J. Phys. Chem.* In press (Part IX).

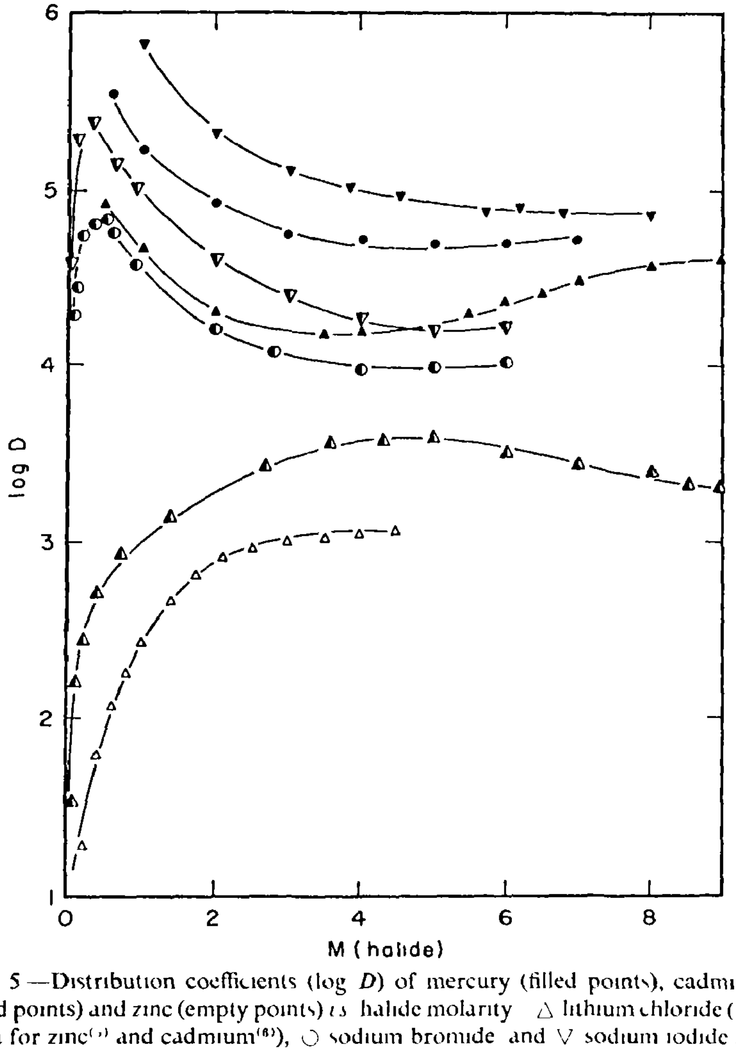


FIG 5—Distribution coefficients (log D) of mercury (filled points), cadmium (half-filled points) and zinc (empty points) *vs* halide molarity △ lithium chloride (published data for zinc[7] and cadmium[6]), ○ sodium bromide and ▽ sodium iodide solutions

A comparison of the anion exchange behaviour of the three IIB group elements zinc, cadmium and mercury in halide solutions, brings out some interesting points (Fig 5) The general trend of the distribution coefficients is D_{Hg} $D_{\mathrm{Cd}} > D_{\mathrm{Zn}}$ for each halide, and $D(\mathrm{I}) > D(\mathrm{Br}) > D(\mathrm{Cl})$ for mercury and cadmium For zinc there are no data for alkali halides, but for the acids the distribution coefficients are very close, with D(HBr) somewhat lower than D(HCl). The cadmium distribution data show maxima in log D vs. M (halide) curves, which are displaced towards lower concentrations the heavier the halide. This behaviour is also obtained with the invasion-corrected curves and reflects the increasing stability of the halide complexes with the atomic number of the halide. There seems to be a good correlation between complex stability and the magnitude of the distribution coefficients for a series of closely related complexes as those discussed here. The trend for the complexes, however, is opposite to that noted for simple anions B such as iodide or perrhenate, where the distribution coefficients are $D_B(I)$ $D_B(Br)$ $D_B(Cl)$. In this case, the reaction involves exchange of B for the halide, which becomes more difficult as the affinity of the halide for the resin increases.$^{(1)}$ The difference in behaviour may indicate that the mechanism of the absorption of the complexes does not involve direct exchange of MX_4^{2-} in solution for X^- in the resin, but rather absorption of neutral MX_2, which then reacts with X^- in the resin the more strongly the higher the complex formation constants.

---

[22] K DAMM and W WEISS, *Z Naturforsch* **10 B**, 535 (1955)

Acknowledgements—The technical assistance of Mrs. N. BAUMAN and Miss S. YITSHAKI is gratefully acknowledged.

J inorg Nucl Chem 1963, Vol 25 pp 875 to 881 Pergamon Press Ltd Printed in Northern Ireland

THE LEWIS-BASE BEHAVIOUR OF SOME HEXA-*n*-ALKYLAMINO TRIPHOSPHONITRILES

T Moeller and S G Kokalis*
Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois

(*Received* 28 *November* 1962)

Abstract -Infra-red and proton magnetic resonance data indicate that the acidic proton in the hexa-amino triphosphonitrile hydrohalides, $N_3P_3(NHR)_6\ HX$ ($X = Cl, Br$), is bonded to a ring imido nitrogen atom rather than to the ring as a whole or to the nitrogen atom of a substituted amino group Additional Lewis-base character is shown by the formation in acetonitrile of specific adducts of the general type $[M^{II}\{N_3P_3(NHR)_6\}_x]^{2+}$ ($R = n\text{-}C_3H_7, n\text{-}C_4H_9$, $x = 1, 2, 6$, $M^{II} = Co^{2+}, Ni^{2+}, Cu^{2+}$) Furthermore, charge-transfer induced alterations in the visible and ultraviolet spectra suggest comparable interaction between the Lewis acid iodine and various hexa-amino triphosphonitriles

Preliminary reports[1,2] on the isolation of monohydrochlorides of the type $N_3P_3(NHR)_6\ HCl$ (R = ethyl, n-propyl, i-propyl, n-butyl, i-butyl) have been verified by the characterization of both the n-propyl and n-butyl compounds and the corresponding hydrobromides These rather distinctive compounds indicate Lewis-base behaviour by the hexa-amino triphosphonitriles Other reported examples of this general property include $N_3P_3F_6\ 2HF\ 2H_2O$,[3] $N_3P_3Cl_6\ HClO_4$,[4] $N_4P_4Cl_8\ 2HClO_4$[4] $N_3P_3Cl_6\ 3SO_3$,[5,6] $N_3P_3Cl_6\ NO_2$,[5] $N_3P_3(NHC_6H_5)_6\ HClO_4$,[4] $N_3P_3(NHC_6H_5)_6\ HCl$[4] $N_3P_3Cl_4(NHCH_3)_2\ HClO_4$,[4] $N_3P_3Cl_4(NHC_2H_4NH_2)_2\ 2HCl$,[1] and $[NP(NH_2)_2\ HC_2H_3O_2]_{3,4}$,[7] On the other hand, spectrophotometric data give no indication of reaction between the trimeric chloride, $N_3P_3Cl_6$, and selected transition-metal halides as acids in acetone or in the fused state [8]

With the halo phosphonitriles, both the ring imido nitrogen atoms and the delocalized d_π-p_π electron system of the ring may serve as potential Lewis-base centres The amido nitrogen atoms of the substituents provide additional potential centres with the amino phosphonitriles

Although potentiometric evaluation of pK_a values for both aqueous and nitrobenzene systems suggests both mono- and diprotonation of the ring imino nitrogen atoms with the hexa-amino triphosphonitriles,[2] definitive evidence that will permit decision among the alternatives is in order Accordingly, infra-red—and proton nuclear magnetic resonance—data have been obtained for several of the monohydrohalides, and interactions with other Lewis acids such as iodine and some dipositive transition-metal ions have been examined. In this connection, the base strengths of the halides $(NPX_2)_{3,4}$ (X = Cl, Br) have been compared with those of the hexa-amino derivatives.

---

* Louderman Chemical Laboratories, Washington University St Louis, Mo

[1] S K Ray and R A Shaw, *Chem and Industr* 1173 (1961)

[2] D Feakins, W A Last and R A Shaw, *Chem and Industr* 510 (1962)

[3] O Schmitz-Dumont and H Kulkens, *Z Anorg Chem* **238,** 189 (1938)

[4] H Bode, K Bulow and G Lienau, *Ber Dtsch Chem Ges* **81,** 547 (1948)

[5] A Besson and M Rosset, *C R Acad Sci, Paris* **143,** 37 (1906)

[6] M Becke-Goehring, H Hohenschutz and R Appel, *Z Naturforsch* **9** B, 678 (1954)

[7] D B Sowerby and L F Audrieth *Ber Dtsch Chem Ges* **94,** 2670 (1961)

[8] B Lakatos, J Bohus and H Arpafi, *Magyar Kem Foly* **67,** 374 (1961)

EXPERIMENTAL

Materials. The hexa-amino triphosphonitriles were prepared as previously described,[9] except recrystallization from n-heptane permitted their quantitative recovery as the hydrohalides. Washing with liquid ammonia, dimethylformamide or water removed the added hydrogen halide to greater or lesser extent. Typical data describing these syntheses are given in Table 1.

TABLE 1. SYNTHESIS AND PROPERTIES OF $N_3P_3(NHR)_6 \cdot HX$

Compound	Yield (%)		Analysis C per cent	H (%)	N (%)	Cl or Br (%)	P (%)	Melting point (°C)
$N_3P_3[NH(CH_2)_2CH_3]_6 \cdot HCl$	96	Calc	41.57	9.44	24.24	6.82	17.87	184
		Found	41.48	9.70	24.20	6.48	17.62	
$N_3P_3[NH(CH_2)_2CH_3]_6 \cdot HBr$	100	Calc	38.30	8.75	22.33	14.16	16.46	154
		Found	38.11	8.71	22.22	13.57	16.35	
$N_3P_3[NH(CH_2)_3CH_3]_6 \cdot HCl$	83	Calc	47.71	10.51	20.87	5.87	15.38	132
		Found	47.78	10.13	20.70	5.66	15.69	

Anhydrous solutions of cobalt (II), nickel (II) and copper (II) perchlorates in tetrahydrofuran (triply distilled from lithium aluminium hydride) and acetonitrile (triply distilled from phosphorus (V) oxide) were obtained by metathesis of anhydrous chloride solutions with silver perchlorate and removal of the precipitated silver chloride.

Measurements. Electrical conductivity was measured at 25°C with an Industrial Instruments bridge Type RC-16B at 1000 c/s, using acetonitrile solutions contained in a glass-stoppered cell ($k = 0.147$ cm^{-1}). All infra-red measurements were made with a Perkin Elmer Model 21 double-beam instrument using a sodium chloride prism. Proton nuclear magnetic resonance spectra were obtained with a Varian A60 instrument, operating at 60 Mc/s with tetramethylsilane as an internal standard.

Absorption spectra were measured with a Cary Recording Quartz Spectrophotometer, Model 14M using either 1 cm or 5 cm quartz cells and 0.001 M acetonitrile or tetrahydrofuran solutions. Interaction between a metal ion and a phosphonitrile was indicated by maximum absorbancy differences at particular mole fractions of metal ion through application of JOB's method of continuous variations.[10,11]

DISCUSSION

That the hydrogen halide is chemically bonded rather than physically trapped is indicated by the fact that the hexa-amino triphosphonitrile hydrohalides can be recrystallized repeatedly from hot heptane without change in composition. On the other hand, the hydrogen halide is removed from the crude reaction product by washing with hot normal N-dimethylformamide, water or liquid ammonia. This suggests that the Lewis-base strength of these substances exceeds that of the hexa-amino triphosphonitriles. Both the immediate reaction of these compounds with silver perchlorate and the comparative conductivity data cited in Table 2 suggest the presence of ionic chloride and of ions of the type $N_3P_3(NHR)_6H^+$. In both respects these compounds are remarkably like the corresponding amine hydrochlorides. Indirectly, this suggests protonation of nitrogen, either in the ring to give $\mathrm{P{=}NH^+}$ or in the *exo* positions to give $\mathrm{P{-}\overset{+}{N}H_2R}$.

---

[9] S. G. KOKALIS, K. JOHN, T. MOELLER and L. F. AUDRIETH, *J. Inorg. Nucl. Chem.* **19**, 191 (1961).

[10] P. JOB, *C. R. Acad. Sci., Paris* **180**, 928 (1925), *Ann. Chim.* (11), **6**, 97 (1936).

[11] W. C. VOSBURGH and G. R. COOPER, *J. Amer. Chem. Soc.* **63**, 437 (1941).

TABLE 2. CONDUCTIVITY OF ACETONITRILE SOLUTIONS AT 25 C

Molarity	Specific Conductivity (ohm^{-1} cm^{-1})			
	$\mathrm{N_3P_3[NH(CH_2)_2CH_3]_6 \cdot HCl}$	$\mathrm{CH_3(CH_2)_2NH_2 \cdot HCl}$	$\mathrm{N_3P_3[NH(CH_2)_3CH_3]_6 \cdot HCl}$	$\mathrm{CH_3(CH_2)_3NH_2 \cdot HCl}$
10^{-3}	8.05×10^{-5}	5.08×10^{-5}	8.65×10^{-5}	4.60×10^{-5}
10^{-4}	1.28×10^{-5}	1.22×10^{-5}	1.37×10^{-5}	1.04×10^{-5}
10^{-5}	0.25×10^{-5}	0.24×10^{-5}	0.19×10^{-5}	0.18×10^{-5}
10^{-6}	0.16×10^{-5}	0.13×10^{-5}	0.07×10^{-5}	0.05×10^{-5}

Both infra-red and proton resonance data are helpful in distinguishing between these possibilities. The significant changes in infra-red spectra (Table 3) on going from the hexa-amino derivative to its hydrochloride are (1) a displacement of the normal 1200 cm^{-1} P=N ring stretching frequency from 1195 cm^{-1} to 1250 cm^{-1} and (2) the appearance of new absorptions in the 915–935 cm^{-1} and 2300–2650 cm^{-1} regions. Both of these favour protonation of a ring nitrogen atom. A hypsochromic shift comparable to the first also characterizes the C=N ring stretching frequency when pyridine is protonated.$^{(12)}$ Furthermore, protonated tertiary amines, such as pyridine, have absorptions for the $=\overset{|}{\mathrm{N}}\mathrm{H}$—group in the 2325–2500, 2500–2600 and 2700 cm^{-1} regions,$^{(13-15)}$ and the other new absorption lies in the 915–935-cm^{-1} region assigned$^{(16)}$ to the P–N–P linkage with no ring resonance. Bonding of a ring nitrogen atom to a proton should eliminate ring resonance, but bonding to an *exo* nitrogen atom should have little effect on the P=N frequency. Any interpretations of protonation of an *exo* nitrogen atom based upon assignments in the –NH$_2$ modes (usual assignments in parentheses in Table 3) were inconclusive because of solvent absorption and ill-defined spectra. As a result of its small steric requirements some bonding of the proton to delocalized ring electrons in the d_π–p_π system may still exist.

Proton resonance data (Table 4) indicate a shift of τ value from 7.7 for amino-group protons of the pure hexa-amino triphosphonitriles to 6.3–6.5 (broad peak) for the hydrochlorides. The profound alteration in electronic environment so indicated cannot be ascribed reasonably to the bonding of a single proton to an —NHR group. However, bonding to a ring nitrogen atom would sufficiently disturb ring resonance to drain electron density away from the amino nitrogen atoms and thus promote enhanced electron density within the ring through π back-donation. The observed shift in τ to lower fields is consistent with this view.

Integrated intensity values for the different proton peaks fail to indicate more than six protons per amino group absorption. Again this suggests bonding to a ring rather than an amino nitrogen atom. If a ring nitrogen atom undergoes protonation, an absorption in a region comparable to that for protonation of the histidine or imidazole ring nitrogen atom (τ = 2.4 to = 2.7)$^{(17)}$ might be expected. Although no

(12) B. WITKOP, *Experientia* **10**, 420 (1954).

(13) D. COOK, *Canad. J. Chem.* **39**, 2009 (1961).

(14) R. F. EVANS and W. KYNASTON, *J. Chem. Soc.* 1005 (1962).

(15) R. C. LORD and R. E. MERRIFIELD, *J. Chem. Phys.* **21**, 166 (1953).

(16) H. H. SISLER, H. S. AHUJA and N. L. SMITH, *Inorg. Chem.* **1**, 84 (1962).

(17) F. A. BOVEY and G. V. D. TIERS, *J. Amer. Chem. Soc.* **81**, 2870 (1959).

TABLE 3 —INFRA-RED DATA FOR HEXA-AMINO TRIPHOSPHONITRILES AND THEIR HYDROCHLORIDES

Compound	System studied	Assignment (cm⁻¹)*					
		Ring P N (1200)	P—N—P (915–935)	NH (2325–2700)	—NH deformation (1500, 1600 2000)	NH bending (780, 820)	—NH rocking (870)
$N_3P_3[NH(CH_2)_2CH_3]_6$	5% (CH_3CN)	1195 *vs*	None	—	—, None	790 *m*	845 *m*
	5% CCl_4	1195 *vs*	915 *m*	None	—, None	—	None
	KBr disk	1183 *vs*	None	None	1625 *m*, None	780 *m*	890 *m*
$N_3P_3[NH(CH_2)_2CH_3]_6$ HCl	5% (CH_3CN)	1260 *s*	925 *m*	—	—, None	790 *w*	None
	5% (CCl_4)	1245 *s*	925 *m*	2640 *w*	—, None	—	None
	5% ($CHCl_3$)	1240 *s*	925 *m*	2650 *w*	1615 *w*, None	—	850 *m*
	KBr disk	1235 *vs*	915 *m*	2300 *w*	1640 *m* None	785 *m*	850 *m*
$N_3P_3[NH(CH_2)_3CH_3]_6$	5% (CH_3CN)	1197 *vs*	None	—	—, None	770 *m*	None
	5% (CCl_4)	1195 *vs*	None	None	— None	—	None
$N_3P_3[NH(CH_2)_3CH_3]_6$ HCl	5% (CH_3CN)	1252 *s*	920 *m*	—	— None	765 *w*	None
	5% (CCl_4)	1245 *s*	935 *m*	2600 *vw*	—, None	—	None
	5% ($CHCl_3$)	1250 *s*	930 *m*	2600 *w*	1610 *vw*, None	—	None
	Nujol mull	1240 *m*	920 *w*	2600 *w*	None None	740 *w*	None
	KBr disk	1240 *m*	915 *w*	2600 *w*	1625 *w* None	770 *w*	None

* *w* = weak (absorbance = 0.0–0.2), *m* = medium (0.2–0.7), *s* = strong (0.7–1.5) — = region of absorption by solvent none = no absorption

TABLE 4.—PROTON MAGNETIC RESONANCE DATA

Compound	τ*	Relative intensity	Number of protons	
			Calculated from intensity	Theoretical
n-$CH_3(CH_2)_2CH_2NH_2$ HCl				
$—CH_3$	9.0	9.5	3.0	3
$—(CH_2)_2—$	8.4	14.0	4.4	4
$CH_2—N$	6.9	7.0	2.2	2
$—NH_3$	1.8	10.0	3.1	3
$N_3P_3[NHCH_2(CH_2)_2CH_3]_6$ HCl				
CH_3	9.1	12.0	18	18
$—(CH_2)_2$	8.6	15.0	23	24
$—CH_2N$	7.1	8.0	12	12
$—NH$	6.5	4.0	6	6 and one H
$N_3P_3[NH(CH_2)_2CH_3]_6$ HCl				
CH_3	9.1	17.5	17.5	18
$CH_2—$	8.4	12.5	12.5	12
$CH_2N—$	7.1	13.0	13.0	12
$NH—$	6.5	6.0	6.0	6 and one H^+
$N_3P_3[NH(CH_2)_2CH_3]_6$ HCl†				
$—CH_3$	9.1	15.0	18.0	18
$—CH_2$	8.5	9.5	12.5	12
$—CH_2N$	7.1	9.5	12.5	12
$—NH$	6.3	4.5	5.4	6
$NH—$	4.2	0.75	0.9	1
$N_3P_3[NH(CH_2)_2CH_3]_6$				
$—CH_3$	9.1	14.0	17	18
$CH_2—$	8.7	10.0	12	12
CH_2N	7.1	10.0	12	12
NH	7.7	5.0	6	6

* Relative to 10.0 for Me_4Si at sweep width of 500 c/s

† This sample as 30 per cent solution in CCl_4, others as 30 per cent in $DCCl_3$

such absorption was visible for $DCCl_3$ solutions, a weak and broad absorption was noted for CCl_4 solutions. The latter (τ −4.2) for the compound $N_3P_3(NH(CH_2)_2CH_3)_6$ HCl, with one-sixth the integrated intensity of the amino proton peak, does support ring protonation. Its absence for deuterochloroform solutions may be as a result of exchange of the acidic proton for the deuteron.

Reports of the co-ordination of acetonitrile and tetrahydrofuran with metal ions (18,19) indicate clearly that interactions with phosphonitrilic compounds can be observed in these media only if such interactions are stronger than those of the solvent molecules. It would be most logical, therefore, to investigate other solvents. However, acetonitrile and tetrahydrofuran are among the few substances that can dissolve both the phosphonitrilic derivatives and anhydrous metal salts without undergoing extensive reaction with the former.

Continuous variations data (Table 5) indicate clearly that interactions between

---

(18) W. HIEBER and J. SEDLMEIER, *Ber. Dtsch. Chem. Ges.* **87**, 25 (1954).

(19) L. I. KATZIN and J. R. FERRARO, *J. Amer. Chem. Soc.* **75**, 3821 (1953).

TABLE 5. CONTINUOUS VARIATIONS STUDY OF PHOSPHONITRILIC HALIDE—LEWIS ACID SYSTEMS

Phosphonitrile	Lewis acid	Concentration (mole/l.)	λ† (mμ)	Observation
$N_3P_3Cl_6$	$Co(CH_3CN)_n^{2+}$	10^{-2}	490, 520	No peak*
	$Co(THF)_n$	10^{-3}	520	No peak, slow formation of $CoCl_4^{2-}$
	$Ni(CH_3CN)_n$	3×10^{-2}	425, 760	No peak
	$Cu(CH_3CN)_n^{+}$	5×10^{-3} 10^{-3}	300, 750	No peak
$N_3P_3Br_6$	$Co(CH_3CN)_n^{2+}$	10^{-2}	490	No peak, formation of $CoBr_4^{2-}$
	$Ni(CH_3CN)_n$	2×10^{-2}	360, 590	Peaks showing bromo-Ni(II) species
	$Cu(CH_3CN)_n^{2+}$	5×10^{-3}	750	No peak, slow formation of $CuBr_n^{2-n}$
$N_4P_4Cl_8$	$Co(CH_3CN)_n^{2+}$	2×10^{-2}	490, 520	No peak, formation of $CoCl_4^{2-}$
	$Cu(CH_3CN)$	5×10^{-3}	755	Formation of $CuCl_4^{2-}$
$N_4P_4Br_8$	$Co(CH_3CN)^{2+}$	10^{-2}	490	No peak, rapid formation of $CoBr_4^{2-}$
	$Ni(CH_3CN)^{2+}$	2×10^{-2}	360, 590	Peaks showing bromo-Ni(II) species
	$Cu(CH_3CN)_n$	5×10^{-3}	750	No peak, rapid formation of $CuBr_n^{2-n}$
$N_3P_3Cl_6$	I_2 in CCl_4	10^{-3}	515	No charge-transfer shift of 515 mμ band, no charge-transfer band in ultra-violet
$N_3P_3Br_6$	I_2 in CCl_4	10^{-3}	515	Same
$N_4P_4Cl_8$	I_2 in CCl_4	10^{-3}	515	Same
$N_4P_4Br_8$	I_2 in CCl_4	10^{-3}	515	Same

* Peak in curve of absorbancy difference vs. mole fraction M-

† Peaks in absorption spectra of solvated Lewis acids that may be expected to change when a new Lewis-base replaces the original solvating molecules.

TABLE 6. CONTINUOUS VARIATIONS STUDY OF HEXAAMINO TRIPHOSPHONITRILE—LEWIS ACID SYSTEMS

Phosphonitrile	Lewis acid	Concentration (mole/l.)	λ† (mμ)	Observation*
$N_3P_3(NHCH_3)_6$	I_2 in $CHCl_3$	10^{-3}	510	Tan solution, peak at 0.5 mole-fraction I_2, new charge-transfer peak at 360 mμ (ε = 730)
$N_3P_3[NH(CH_2)_2CH_3]_6$	I_2 in CCl_4	10^{-3}	515	Tan solution, peak at 0.5–0.7 mole-fraction I_2, new charge-transfer peak at 375 mμ (ε = 1500)
	$Co(CH_3CN)_n^{2+}$	10^{-2}	490	Yellow solution, peak at 0.25 mole-fraction Co^{2+} (ε = 144)
	$Ni(CH_3CN)_n^{2+}$	2×10^{-2}	360, 590	Yellow solution, peaks at 0.35–0.50 (ε = 91.5) and 0.75–0.80 (ε = 27.5) mole-fraction Ni^{2+}. Intense peak at 270 mμ (ε = 1000)
	$Cu(CH_3CN)_n^{2+}$	5×10^{-3}	755	Yellow solution, peaks at 0.30 (ε = 95) and 0.50 (ε = 41) mole-fraction Cu^{2+}
			235	Yellow solution, peaks at 0.30 (ε = 240) and 0.50 (ε = 160) mole-fraction Cu^{2+}
$N_3P_3[NH(CH_2)_3CH_3]_6$	$Co(CH_3CN)_n^{2+}$	10^{-2}	490	Yellow solution, peak at 0.20–0.25 mole-fraction Co^{2+} (ε = 380)
$N_3P_3[N(CH_3)_2]_6$	I_2 in CCl_4	10^{-3}	510	Tan solution, peak at 0.50 mole-fraction I_2, new charge-transfer peak at 380 mμ (ε = 730)

* ε values in l. $mole^{-1}$ cm^{-1}.

† Peaks in absorption spectra of solvated Lewis acids that may be expected to change when a new Lewis base replaces the original solvating molecules.

TABLE 7 —INFRA-RED SPECTRA OF PHOSPHONITRILE LEWIS ACID SYSTEMS

Phosphonitrile	Lewis acid	Concentration	Absorption (cm $^{-1}$)	Alteration of spectrum
$N_3P_3Cl_6$	I_2 in CCl_4	10^{-3} M	1220	None, even with 10 mole excess of I_2
	$AgClO_4$ in C_6H_6	5%	1210	None
$N_3P_3Br_6$*	$AgClO_4$ in C_6H_6	5%	1177	None, even with 10 mole excess of $AgClO_4$
$N_4P_4Cl_8$	$AgClO_4$ in C_6H_6	5%	1310	None
$N_4P_4Br_8$*	$AgClO_4$ in C_6H_6	5%	1270	None
$N_3P_3[NH(CH_2)_2CH_3]_6$	I_2 in CCl_4	10^{-3} M	1195	None, even with 10 mole excess of I_2
$N_3P_3[NH(CH_2)_3CH_3]_6$	$AgClO_4$ in C_6H_6	10^{-3} M	1195	None

* Extensive precipitation of AgBr, no AgCl in chloride systems

Co^{2+}, Ni^{2+}, or Cu^{2+} ions and the ring systems of the trimeric and tetrameric phosphonitrilic chlorides and bromides are too weak to displace solvent molecules. Rather it appears that slow solvolysis of the halide occurs with subsequent addition of released halide ions to the coordination sphere of the metal ion. Rate of colour development indicates qualitatively that rate of solvolysis decreases as $(NPBr_2)_n > (NPCl_2)_n$ and as $n = 4 > n = 3$ (X = same). Even iodine, which is less likely to react with released halide ion, gave no spectrophotometric evidence of the formation of a charge-transfer complex species (Table 7).

On the other hand, the amino phosphonitriles do act as Lewis bases toward metal ions and iodine (Table 6). The difference may lie in the ability of the halogen atoms to decrease ring electron density. Analogously, although benzene acts as a Lewis base, the perfluoro compound C_6F_6 is a Lewis acid.(20) Electron donor substituents such as amines may be expected to have the opposite effect and thus enhance the donor capacity of the ring or of the ring nitrogen atoms. It is apparent, of course, that the exact donor centres can be established only through more detailed studies (e.g., through crystal-structure determination).

Acknowledgement: Support received by S. G. K. in the form of graduate fellowships from the Ethyl Corporation and E. I. du Pont de Nemours and Company is gratefully acknowledged.

(20) C. R. PATRICK and G. S. PROSSER, *Nature, Lond.* **187**, 1021 (1960).

J Inorg Nucl Chem, 1963, Vol 25, pp 883 to 892 Pergamon Press Ltd Printed in Northern Ireland

BIDENTATE ORGANOPHOSPHORUS COMPOUNDS AS EXTRACTANTS*—I

EXTRACTION OF CERIUM, PROMETHIUM, AND AMERICIUM NITRATES

T H SIDDALL, III
Savannah River Laboratory E I du Pont de Nemours & Co
Aiken, South Carolina

(*Received* 19 *October* 1962)

Abstract It is shown that tetraalkyl methylenediphosphonates $[(RO-)_2\overset{O}{\overset{\|}{P}}-CH_2-\overset{O}{\overset{\|}{P}}(-OR)_2]$, dialkyl N,N-dialkylcarbamylphosphonates $[(RO-)_2\overset{O}{\overset{\|}{P}}-\overset{O}{\overset{\|}{C}}-N(-R)_2]$ and dialkyl N,N-dialkylcarbamylmethylenephosphonates $[(RO-)_2\overset{O}{\overset{\|}{P}}-CH_2-\overset{O}{\overset{\|}{C}}-N(-R)_2]$ are powerful, chelating extractants for cerium, promethium, and americium from solutions of nitric acid

TRIVALENT lanthanides and actinides are only poorly extracted from nitric acid solutions by monodentate compounds such as tri-n-butyl phosphate (TBP) Yet the highly acidic waste concentrates from such processes as the Purex process are important potential sources of radioisotopes of these elements The poor extraction ability of the organophosphorus esters for these elements is due to back-salting by nitric acid that is extracted at the same time One approach to improving extractant strength is to alter the molecular structure in a manner that will improve the extraction of these metals relative to that of acid

The obvious approach to increasing the relative extraction of these metals is to employ bidentate extractants that are capable of chelation Already BANKS *et al*,[1] have synthesized tetrahexylmethylenediphosphine oxide, $(C_6H_{13}-)_2\overset{O}{\overset{\|}{P}}-CH_2-\overset{O}{\overset{\|}{P}}(-C_6H_{13})_2$, and have shown that extraordinarily strong extraction of uranium (VI) is obtained with this compound However, HEALY and KENNEDY[2] were unable to observe an increase in the extraction of uranium (VI) by tetrabutyl methylenediphosphonate (TBMDP), $(C_4H_9O-)_2\overset{O}{\overset{\|}{P}}-CH_2-\overset{O}{\overset{\|}{P}}(-OC_4H_9)_2$, as compared to extraction by analogous monofunctional compounds Our preliminary investigations also failed to show any extraordinary extraction of uranium by TBMDP However, poor material balance of uranium was observed in this Laboratory which indicates that the TBMDP may not be completely soluble in benzene for the conditions in the test performed by HEALY and KENNEDY In any event when tetrahexyl methylenediphosphonate was substituted for the butyl ester, uranium was extracted much more strongly than by monodentate analogues This might be expected on the basis that the higher molecular weight of the hexyl ester would make it soluble in benzene even if the butyl ester were not Further experiments with uranium extraction were postponed in favour of work with trivalent lanthanides and actinides The purpose of this paper is to report the results of the earlier phases of this work It is planned that this shall be the first of several papers concerning the behaviour of bidentate extractants As such, it will be only in the nature of an introduction to the extraction of trivalent lanthanides and actinides Later papers will cover details of mechanisms, a wider variety of organic structures, a wider range of extraction variables, and extraction of a diversity of elements

---

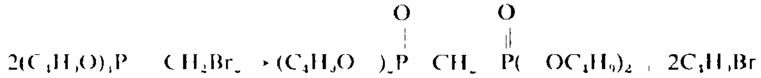
* The information contained in this article was developed during the course of work under contract AT(07-2)-1 with the U S Atomic Energy Commission

(1) J J RICHARD, K E BURKE, J W O LAUGHLIN and C V BANKS, *J Amer Chem Soc* **83**, 1722-6 (1961)

(2) T V HEALY and J KENNEDY, *J Inorg Nucl Chem* **10**, 128-36 (1959)

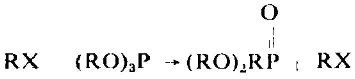
PREPARATION OF MATERIALS AND EXPERIMENTAL PROCEDURES

The diphosphonates carbamylphosphonates $[(RO)_2\overset{O}{P}—\overset{O}{C}—N(R)_2]$ and carbamylmethylenephosphonates $[(RO)_2\overset{O}{P}CH_2\overset{O}{C}N(R)_2]$, used in this work were all prepared by the Arbuzov rearrangement For example,


$$2(C_4H_9O)_3P + CH_2Br_2 \rightarrow (C_4H_9O)_2\overset{O}{P}CH_2\overset{O}{P}(OC_4H_9)_2 + 2C_4H_9Br$$

Yields of about 40 per cent of the second and third classes of compounds were readily obtained by rapidly adding the carbamyl chloride, $R_2N\overset{O}{C}Cl$, or chloroacetamide, $R_2N\overset{O}{C}CH_2Cl$, to an equimolar quantity of trialkyl phosphite that was already heated to about 200 C The course of the reaction was followed by observing the distillation of by-product RCl About 15 min was required to complete the reaction to the point where distillation had dropped to a very slow rate At this point the reaction flask was removed from the heating bath in order to minimize the exposure of product to high temperatures

The preparation of the diphosphonates, especially tetrabutyl methylenediphosphonate, is complicated by the fact that by-product alkyl halide cannot be removed with great rapidity from the reaction flask (See article by CADE(8) for a discussion of this problem) Since dibromides or diiodides must be used as starting materials, by-product bromides or iodides are formed and these are about as reactive as the starting dihalide The result is a substantial loss of yield to the isomerization reaction,


$$RX + (RO)_3P \rightarrow (RO)_2R\overset{O}{P} + RX$$

The best results were obtained in this Laboratory by the following procedure

(1) Add one-half mole of phosphite to one mole of alkyl dibromide at reflux and heat over night The reaction flask is fitted with a fractionating column and the heating rate is set such that very slow distillation takes place

(2) The fractionating column is removed and the reaction flask is heated strongly to drive off excess alkyl dibromide and by-product alkyl bromide

(3) A further one-half mole of phosphite is added slowly with the heating bath at 180–200°C After by-product distillation slows (total time about one hour), the reaction is considered complete

(8) J A CADE, *J Chem Soc* 2266–72 (1959)

For the tetrabutyl ethylenediphosphonate and the propylene- and butylenediphosphonates, yields of 40 per cent can be obtained (based on phosphite) With TBMDP the fractionating column cannot be used effectively in step (1) since methylene dibromide and butyl bromide have nearly the same boiling point Yields of TBMDP were 20–30 per cent Dibutyl butylphosphonate was obtained from the Virginia-Carolina Chemical Co

All extractants were distilled under high vacuum After distillation, they were made up to 0 5 M in benzene and stirred with 6 M HCl at 60°C for 4 hr The benzene solutions were then washed with water, a solution of sodium hydroxide, and twice more with water Immediately after washing, the benzene was evaporated off and the extractants pumped down under high vacuum This is essentially the procedure recommended by PEPPARD *et al* (1)

In one trial the treatment with HCl was omitted with a sample of TBMDP Extraction of cerium with this sample went through a minimum at about 0 1 M HNO_3 in the aqueous phase and then rose to high values at lower acidity Evidently the treatment with HCl destroys some acidic impurity (or its parent compound) that would otherwise invalidate results obtained at low acidity Such impurities would be expected because of the high temperatures required to synthesize and distill these compounds As a further precaution the tracer solutions were made up to contain 0 003 M $Ce(NO_3)_3$ on the possibility that very low levels of impurities might be present and that they would be saturated by this concentration of cerium

The failure to include the purification step with HCl or a similar step, may account for the high extraction coefficients obtained by SAISHO(5) with tetrabutyl ethylene-1,2-diphosphonate

Equilibrations of 1 min duration were performed with a small electric stirrer At three widely spaced points on the extraction curve, the attainment of equilibrium was tested by approaching equilibrium first with cerium initially in the aqueous phase and then repeated by having cerium initially in the organic phase Satisfactory agreement (3 per cent mean deviation) was obtained in all cases except with dibutyl butylphosphonate and tetrabutyl butylene-1 4-diphosphonate Above about 8 0 M nitric acid in the aqueous phase both of these compounds gave some evidence of slow equilibria This phenomenon was not investigated further since neither of these compounds were of principal interest to the study For this reason no data are reported for these two compounds at high HNO_3 concentrations in the aqueous phase

^{241}Am, ^{144}Ce and ^{147}Pm were determined by conventional counting procedures When the three elements were present in the same solution, ^{144}Ce and ^{147}Pm were determined by differential β-counting and ^{241}Am bx α-counting Small mounts (usually 25 μl) of the organic phase were made in order to minimize the problem of volatilizing these high boiling extractants and obtaining clean plates for α-counting Even so it was often necessary to prepare several plates in order that at least two could be obtained that were relatively clean Mounts of the organic phase probably are the limiting source of error for the data for americium A mean deviation of about 5 per cent in α-counting was obtained between duplicates The extraction coefficients for cerium were generally determined with about 3 per cent mean deviation The mean deviation for data with promethium was about 6 per cent, since they involved a determination by differences However as extraction coefficients approached 10^2, precision fell to about 10 15 per cent, and at 10^3 precision was only within a factor of about two This decrease in precision was apparently due to inability to obtain sufficiently complete separation of aqueous from organic phases even though the phases were centrifuged

Water analyses were performed by the Karl Fischer method Acidity was determined by ordinary acid-base titration Densities were obtained by weighing 1-ml micropipettes filled with extractant

RESULTS AND DISCUSSION

Data for the extraction of metals at 30°C are given in Figs 1 and 2 and repeated in Table 1 Data for the extraction of nitric acid at 30°C are given in Table 2 Densities and the composition of the extractant phase at 23°C are given in Table 3 for all of the extractants One set of data in Table 3 is given for organic samples that had been

---

(1) D F PEPPARD, G W MASON and J L MAIER, *J Inorg Nucl Chem* 3, 215–28 (1956)

(5) H SAISHO, *Bull Chem Soc Japan* **34**, 859–61 and 1254 57 (1961)

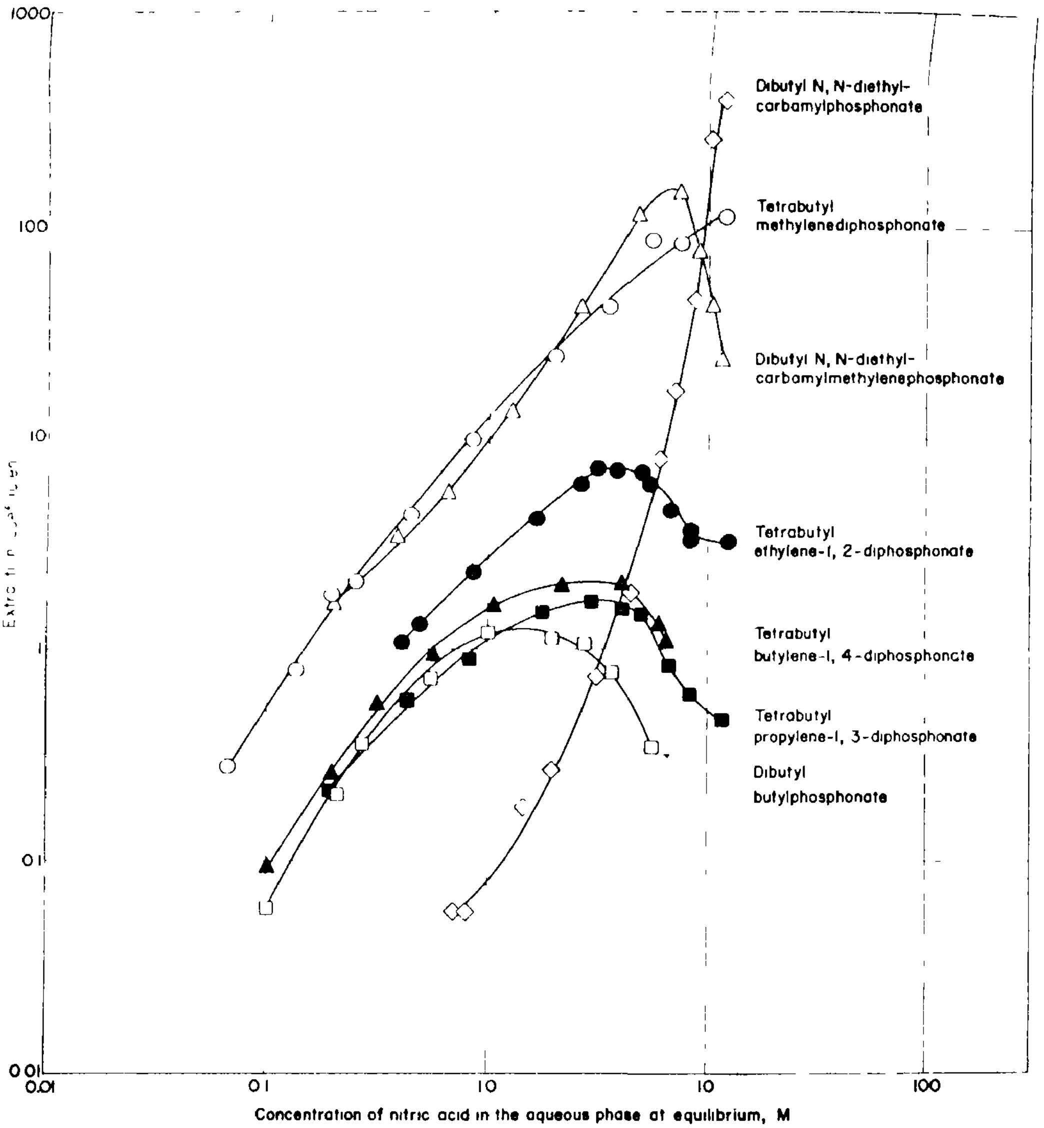


Fig 1 --Extraction of cerium at 30 C by various bidentates and by dibutyl butyphosphonate

equilibrated with water, the other set is for samples that were in equilibrium with 6 5 M nitric acid The data in all the tables and figures are for undiluted extractant

The data of the first two tables and figures indicate that the bidentate extractants that can form five or six membered rings with Ce, Pm, and Am are chelating extractants Extraction coefficients are approximately 100 times as large over most of the acidity range as those obtained with monodentates However, in the diphosphonate series, extraction decreases sharply as additional bridging methylene groups are introduced between the phosphoryl groups

It is true that both the propylene (TBPDP) and butylene (TBBDP) compounds are still slightly more powerful extractants than is dibutyl butylphosphonate (DBBP)

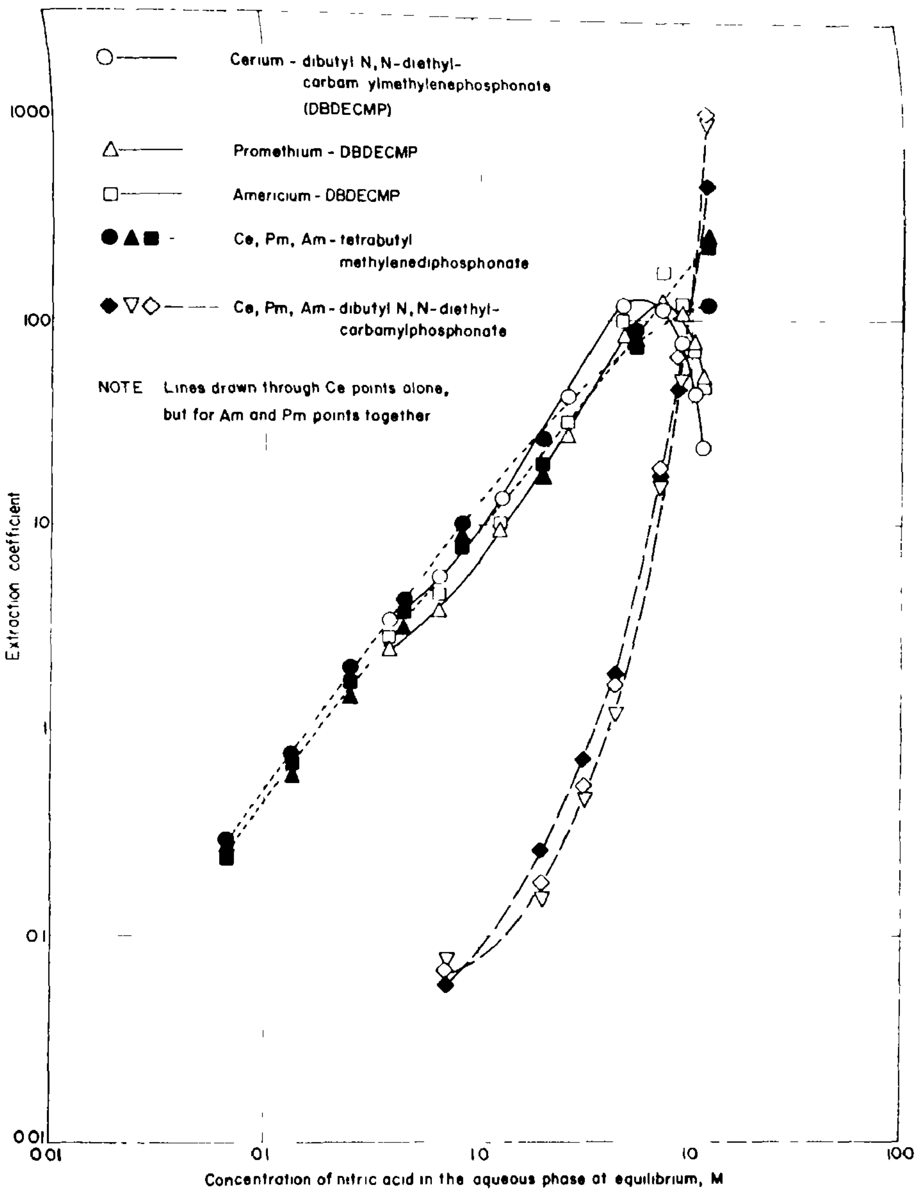


Fig. 2 Extraction of cerium, promethium, and americium at 30 C by three bidentate extractants

The order of extractant strength is TBBDP TBPDP DBBP The greater extractant strength of the diphosphonates may be explained as due to the higher concentration of phosphoryl groups in these compounds By that token one would expect the order to be TBPDP > TBBDP > DBBP Possibly, in the TBBDP molecule, since the phosphoryl groups are farther apart, they have less of the effect of being electronegative substituents on each other This may offset the slightly higher concentration of phosphoryl groups in TBPDP However, even with the butylenediphosphonate, the two phosphoryl groups are not far enough apart to be completely

TABLE 1 —EXTRACTION OF CERIUM, PROMETHIUM AND AMERICIUM NITRATES AT 30 C UNDILUTED EXTRACTANTS

Dibutyl N N-diethylcarbamylphosphonate				Dibutyl N N-diethylcarbamylmethylene-phosphonate				Tetrabutyl methylenediphosphonate			
Nitric acid aqueous phase, (M)	Extraction coefficient			Nitric acid aqueous phase (M)	Extraction coefficient			Nitric acid aqueous phase (M)	Extraction coefficient		
	Ce	Pm	Am		Ce	Pm	Am		Ce	Pm	Am
11.6	24.7	53	48	12.0	440	900	1000	12.0	120	250	240
10.5	44	78	76	10.3	260			7.4	86		
9.0	78	105	118	8.7	48	51	68	5.5	91	81	78
7.3	118	119	161	7.2	17.6	16	19	3.5	43		
4.74	118	83	99	6.0	8.2			2.00	27	17	20
2.60	43	27	32	4.48	1.85	1.2	1.7	0.83	10.2	8.8	7.8
1.28	13.8	9.5	10	3.14	0.72	0.47	0.53	0.44	4.4	3.0	3.7
0.65	5.6	3.8	4.6	1.98	0.26	0.15	0.18	0.25	2.0	1.4	1.7
0.38	3.4	2.4	2.8	1.47	0.180	0.136	0.125	0.196	1.82		
0.20	1.7			0.78	0.059			0.134	0.77	0.59	0.69
				0.70	0.058	0.077	0.069	0.066	0.29	0.28	0.24

Tetrabutyl butylene-1 4-diphosphonate		Tetrabutyl propylene-1 3-diphosphonate		Tetrabutyl ethylene-1 2-diphosphonate		Dibutyl butylphosphonate	
Nitric acid, aqueous phase, (M)	Extraction coefficient	Nitric acid, aqueous phase, (M)	Extraction coefficient	Nitric acid, aqueous phase, (M)	Extraction coefficient	Nitric acid aqueous phase (M)	Extraction coefficient
	Ce		Ce		Ce		Ce
6.5	1.12	11.9	0.47	12.2	3.3	5.5	0.35
6.0	1.32	8.3	0.62	8.4	3.3	3.67	0.78
4.09	2.07	6.7	0.85	8.3	3.8	2.73	1.08
2.12	2.00	5.0	1.50	6.7	4.7	1.96	1.12
1.05	1.60	4.11	1.60	5.4	6.2	1.00	1.21
1.00	1.60	2.98	1.72	5.0	7.1	0.55	0.73
0.56	0.94	1.76	1.51	3.88	7.2	0.271	0.36
0.312	0.55	0.83	0.90	3.11	7.3	0.196	0.211
0.196	0.259	0.431	0.58	2.62	6.2	0.100	0.060
0.100	0.094	0.196	0.215	1.65	4.2		
				0.85	2.36		
				0.49	1.32		
				0.405	1.10		

Table 2 —Extraction of nitric acid at 30 C undiluted extractants

Dibutyl N,N-diethylcarbamylphosphonate		Dibutyl N N-diethylcarbamylmethylenephosphonate		Tetrabutyl methylenediphosphonate		Tetrabutyl ethylene-1,2-diphosphonate	
Nitric acid (M)		Nitric acid (M)		Nitric acid (M)		Nitric acid (M)	
Aqueous phase	Organic phase	Aqueous phase	Organic phase	Aqueous phase	Organic phase	Aqueous phase	Organic phase
12 1	8 1	12 3	6 18	11 8	5 4	12 4	5 7
9 0	6 0	8 6	4 50	8 3	4 3	8 4	4 37
5 6	4 20	5 1	2 87	4 53	2 93	4 54	3 09
3 69	3 02	3 36	2 02	2 34	1 86	3 06	2 36
1 58	1 61	1 01	0 67	1 10	1 01	1 00	1 01
1 00	1 11	0 98	0 65	0 60	0 60	0 56	0 56
0 95	1 07	0 483	0 262	0 341	0 320	0 302	0 276
0 55	0 66	0 216	0 068	0 190	0 140	0 176	0 126
0 305	0 366	0 068	0 009	0 093	0 057	0 089	0 048
0 166	0 186						
0 098	0 100						

Tetrabutyl propylene-1,3-diphosphonate		Tetrabutyl butylene-1,4-diphosphonate		Dibutyl butylphosphonate	
Nitric acid (M)		Nitric acid (M)		Nitric acid (M)	
Aqueous phase	Organic phase	Aqueous phase	Organic phase	Aqueous phase	Organic phase
12 3	5 9	12 3	5 9	12 4	5 1
8 5	4 47	8 5	4 34	8 3	3 69
4 80	3 28	4 60	3 20	4 22	2 77
3 24	2 50	3 00	2 40	2 94	2 28
1 17	1 21	1 21	1 32	1 19	1 24
1 01	1 07	1 00	1 14	1 01	1 11
0 54	0 63	0 57	0 70	0 60	0 71
0 298	0 331	0 329	0 392	0 355	0 396
0 178	0 169	0 206	0 219	0 214	0 188
0 106	0 080	0 129	0 114	0 120	0 075

TABLE 3 — COMPOSITIONS OF VARIOUS ORGANIC PHASES

Compound	HNO_3 (M)		H_2O (M)	Density	Mole ratio	
	Aqueous	Organic	Organic		HNO_3/Compound	H_2O/Compound
Tetrabutyl methylenediphosphonate	0	0	7.4	1.033		3.3
	6.5	3.76	2.9	1.111	1.84	1.4
Tetrabutyl ethylene-1,2-diphosphonate	0	0	8.3	1.025		3.9
	6.5	3.82	2.5	1.105	1.94	1.3
Tetrabutyl propylene-1,3-diphosphonate	0	0	10.1	1.023		5.1
	6.5	3.79	2.5	1.106	1.97	1.3
Tetrabutyl butylene-1,4-diphosphonate	0	0	9.6	1.020		5.0
	6.5	3.81	2.6	1.101	2.07	1.4
Dibutyl N,N-diethylcarbamylphosphonate	0	0	3.4	1.020		1.1
	6.5	3.52	4.3	1.094	1.30	1.6
Dibutyl N,N-diethylcarbamylmethylenephosphonate	0	0	17.9	1.025		7.8
	6.5	4.59	5.8	1.132	1.90	2.4
Dibutyl butylphosphonate	0	0	4.6	0.952		1.4
	6.5	3.35	1.1	1.026	1.10	0.36

independent of each other As shown in Table 3, the ratio of moles of nitric acid extracted per mole of phosphoryl group is not as high as that obtained with dibutyl butylphosphonate One explanation is that, even when separated by four methylene groups, phosphoryl groups still act as electronegative substituents on each other Electronegative substituents are known to reduce extractant strength The data for water extraction also show that the phosphoryl groups of the bidentate compounds do not act independently

As far as can be deduced from the data in this paper, extraction by TBMDP and by dibutyl N,N-diethylcarbamylmethylenephosphonate (DBDECMP), aside from chelation, follows the same general type of mechanism as that encountered with ordinary organophosphorus esters A neutral molecule of metal nitrate is complexed by extractant in the organic phase Any decrease in slope of the extraction curves with increasing concentration of nitric acid can be interpreted as the result of increased back-salting as more nitric acid is extracted The ratio of acid to metal extraction is greater for DBDECMP than it is for TBMDP As a consequence, the extraction curve for the metals with DBDECMP actually passes through a maximum while the slopes with TBMDP decrease only moderately, if at all

On the other hand, it would be hard to say that extraction with dibutyl N,N-diethylcarbamylphosphonate (DBDECP) follows this same general mechanism Extraction with DBDECP shows an exponential rise with increasing acidity In fact a good straight line is obtained when extraction coefficients are plotted against aqueous acidity on semilog paper Back-salting by nitric acid is offset by some new factor A simple explanation is that metal extraction by the carbamylphosphonate is based on an anion mechanism,

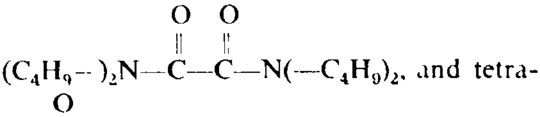
$$M^{3+} + (3 + x)NO_3^- + xH^+ + y(\mathrm{DBDECP}) \quad H_xM(NO_3)_{3+x}(\mathrm{DBDECP})_y$$

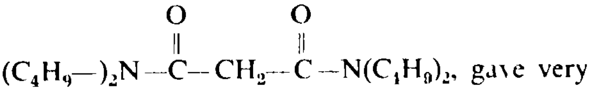
Further experiments now in progress and to be reported in a later paper indicate that the choice of a mechanism of this type is correct

The data of Fig 2 indicate that there is a tendency for the relative order of extraction of metals to change as the concentration of nitric acid changes At low concentrations the order is Ce > Am ≃ Pm, but at high concentrations the order is Am ≃ Pm > Ce The effect is small and no explanation is obvious

The question arises as to what other electron-donating groups might serve as the functional groups in chelating bidentates for the extraction of trivalent lanthanides and actinides Preliminary experiments in this Laboratory show that strong extractants can be obtained by including a carbonyl group and a phosphoryl group in the same molecule Unfortunately pure samples of carbonylphosphonates were not obtained in the synthesis of these compounds The Perkow Reaction appears to be a competitive reaction with the Arbuzov rearrangement, which leads to a difficult problem in purification Further investigations of the synthesis are planned

Diamides do not seem to be chelating extractants for these trivalent lanthanides and actinides Both tetrabutyl oxalamide, $(C_4H_9-)_2N-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-N(-C_4H_9)_2$, and tetrabutyl malonamide, $(C_4H_9-)_2N-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-N(C_4H_9)_2$, gave very low extraction





coefficients for cerium from 12 M HNO_3 Chemical analysis, proton magnetic resonance spectra and infra-red spectra indicated that a fairly pure sample of the oxalamide was obtained, however, the malonamide contained some unidentified impurity The failure of these diamides to act as chelating extractants is rather surprising in view of the effectiveness of the amide group in the carbamylphosphonates and carbamylmethylenephosphonates No explanation is readily apparent for this behaviour

In conclusion it is seen that very powerful bidentate extractants can be obtained for the trivalent lanthanides and actinides These extractants or their homologues promise to have practical utility for the recovery of these elements from a variety of sources such as the high activity waste of the Purex process The extractants whose behaviour is reported in this paper probably have about as low a molecular weight as can be useful, tetraethyl methylenediphosphonate, for example, is water soluble Even larger molecules than those studied here may be desirable Tetrabutyl methylenediphosphonate is limited in usefulness as an extractant when diluted with n-dodecane because the dilutions form two organic phases when contacted with a variety of aqueous phases Higher homologues such as the tetraamyl and tetrahexyl esters may be diluted without encountering serious problems from the formation of two organic phases The higher homologues are easily synthesized, but their purification is complicated by progressively higher boiling points

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 893 to 904. Pergamon Press Ltd. Printed in Northern Ireland

NOTES

Hafnyl triphosphates

(*Received* 12 *October* 1962)

IN PREVIOUS communications, it was pointed out the complexing ability of sodium triphosphate with many substances specially rare-earths⁽¹⁾, thorium⁽²⁾, uranyl⁽³⁾ and others.

In many cases, it was not possible to isolate the compounds which were therefore detected by many ways: potentiometric, conductometric, spectrophotometric, etc.

The compounds formed when sodium triphosphate reacts with zirconyl ions were already described⁽³⁾.

The behaviour of hafnium and hafnyl ions with sodium triphosphate is now investigated, by using the same procedure outlined in the case of zirconium. We observe that hafnium and hafnyl compounds by the reaction with sodium triphosphate show the same behavior that zirconium and zirconyl compounds, the potentiometric and conductometric curves are very similar.

The compounds which were isolated were all white amorphous powders, as was pointed out by the X-ray diffraction patterns.

Experimental

(1) *Sodium triphosphate*, $Na_5P_3O_{10}\cdot6H_2O$, was prepared from anhydrous sodium triphosphate, supplied by the Victor Chemical Trading Corporation, and purified according to a procedure described by WATTERS *et al.*⁽⁴⁾

(2) *Hafnyl chloride*, $HfOCl_2\cdot8H_2O$—The product obtained by the reaction of hafnium oxide (Johnson Matthey and Co. Ltd., Spectrographically pure) with a mixture of Hf/H_2SO_4 in a platinum crucible was diluted with water. The precipitate obtained by the addition of dil. ammonium hydroxide was filtered off, washed with water until free of sulphate and then dissolved in concentrated hydrochloric acid. The resulting solution was evaporated near to dryness and the hafnyl chloride was purified by dissolving in a little amount of water, conc. hydrochloric acid added and evaporated again. The resulting crystals were filtered off, well pressed and washed with acetone.

(3) *Hafnium* (IV) *sulphate*, $Hf(SO_4)_2,4H_2O$, was prepared in the same way as the zirconium sulphate, according to a procedure described by CLABAUGH and GILCHRIST.⁽⁵⁾

(4) $(HfO)_5(P_3O_{10})_2\cdot2Na_5P_3O_{10}\cdot12H_2O$ (I). A solution of 1.32 g of hafnium sulphate in 15 ml of water was added, under stirring, to a solution of 2.86 g of sodium triphosphate in 20 ml water. A solution was obtained after one hour of continuous stirring. Gradually a white gelatinous precipitate was formed and after one week it was centrifugated, washed with 3 portions of 10 ml water and then dried in a vacuum desiccator over calcium chloride until constant weight.

Analysis: $(HfO)_5(P_3O_{10})_2\cdot2Na_5P_3O_{10}\cdot12H_2O$ (2430.9)
Hf calc. 36.73 found 36.21
P calc. 15.29 found 15.72
H_2O calc. 8.89 found 9.01

(5) $(HfO)_2NaP_3O_{10}\cdot4H_2O$ (II). A solution of 0.96 g of sodium triphosphate in 20 ml water was slowly added, under stirring, to a solution of 1.64 g hafnyl chloride in 20 ml water. The stirring was

---

⁽¹⁾ A. G. BUYERS, F. GIESBRECHT and L. F. AUDRIETH, *J. Inorg. Nucl. Chem.* **5**, 133 (1957); F. GIESBRECHT and L. F. AUDRIETH, *J. Inorg. Nucl. Chem.* **6**, 308 (1958); F. GIESBRECHT, *J. Inorg. Nucl. Chem.* **15**, 265 (1960).

⁽²⁾ E. GIESBRECHT and G. VICENTINI, *Anais assoc. brasil. quim.* **19**, 61 (1960).

⁽³⁾ E. GIESBRECHT and G. VICENTINI, *Anais assoc. brasil. quim.* **18**, 63 (1959).

⁽⁴⁾ J. I. WATTERS, E. D. LOUGHRAN and S. M. LAMBERT, *J. Amer. Chem. Soc.* **78**, 4855 (1956).

⁽⁵⁾ W. S. CLABAUGH and R. GILCHRIST, *J. Amer. Chem. Soc.* **74**, 2104 (1952).

maintained for 15 min, the white gelatinous precipitate was filtered off, dried over calcium chloride and then finely ground. The resulting powder was washed with 3 portions of water and dried until constant weight in a vacuum desiccator over calcium chloride.

Analysis $(HfO)_2NaP_3O_{10}\cdot 4H_2O$ (737.2)

Hf	calc	48.70	found	48.91
P	calc	12.60	found	12.83
H_2O	calc	9.77	found	9.46

(6) $(HfO)_5(P_3O_{10})_2\cdot 12H_2O$ (III). A solution of 2.05 g of hafnyl chloride in 20 ml water was slowly added under stirring to a solution of 0.95 g sodium triphosphate in 20 ml water. The white gelatinous precipitate was centrifugated and washed with 4 portions of 5 ml water. It was dried over conc. sulphuric acid, finely grinded, washed with 5 portions of 15 ml water, and dried, until constant weight, in a vacuum desiccator over calcium chloride.

Analysis $(HfO)_5(P_3O_{10})_2\cdot 12H_2O$ (1 695.0)

Hf	calc	52.68	found	52.19
P	calc	10.96	found	10.79
H_2O	calc	12.75	found	12.96

(7) *Analysis procedure.*—Phosphorus and hafnium were determined after fusion of the substance with a mixture of sodium and potassium carbonates. The melted was poured into water and the resulting precipitate, after filtering and washing, was dissolved in sulphuric acid, the hafnium precipitated as

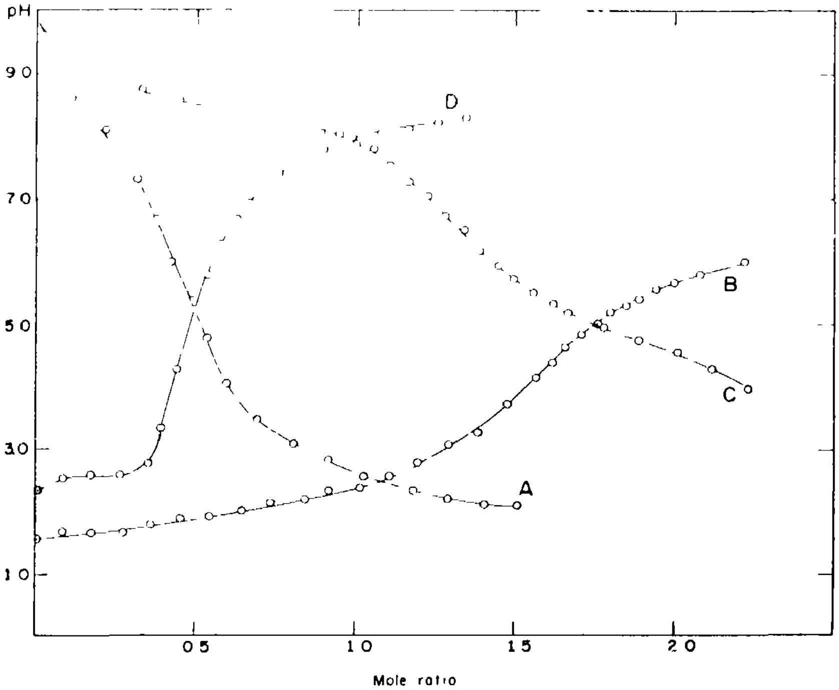


Fig. 1.—pH Titrations

A—Titration of 10 ml 0.05M sodium triphosphate with 0.05M hafnium sulphate. Precipitation occurred after the 0.5 mole ratio was exceeded.

B—Titration of 10 ml of 0.05M hafnium sulphate with 0.05M sodium triphosphate. Precipitation occurred at the beginning of the titration.

C—Titration of 10 ml of 0.05M triphosphate with 0.05M hafnyl chloride. Precipitation occurred after the 0.5 mole ratio was exceeded.

D—Titration of 10 ml of 0.05M hafnyl chloride with 0.05M sodium triphosphate. Precipitation occurred at the beginning of the titration.

hafnium hydrogen phosphate, and ignited to the pyrophosphate The above filtrate was acidified with hydrochloric acid, boiled for 30 min and the resulting phosphate precipitated by the usual way as magnesium ammonium phosphate and ignited to the magnesium pyrophosphate

The water determination was carried out by the loss of weight of the substance by ignition to 800–900°C,

(8) All pH measurements were made with the Metrohm potentiometer, model E 148c, using a combined glass-satured calomel electrode

(9) Conductivity measurements were carried out with the aid of a line operated Conductivity Bridge, model RC-16B from the Industrial Instruments Inc, using platinum platinized electrodes The cell constant was not determined since conductance values were relative throughout a given titration

Discussion and Results

A—pH *Titrations*

(1) The titration of 0 05M sodium triphosphate solution with hafnium sulphate solution of the same concentration showed the formation of a soluble complex in which the ratio Hf^{4+} $P_3O_{10}^{5-}$ is 1 2 (Fig 1-A) *These solutions are not stable, after some days a white gelatinous precipitate* is observed, which was isolated and analysed Its formula is $(HfO)_5(P_3O_{10})_2\,2Na_5P_3O_{10}\,12H_2O$ (I) Its formation, in the above case, can be explained by the hydrolysis of the ion Hf^{4+} to HfO^{2+}

The existence of a compound with the ratio $5HfO^{2+}$ $4P_3O_{10}^{5}$ could also be detected in the potentiometric titration of sodium triphosphate solutions with hafnyl chloride solutions (Fig 1-C)

(2) The potentiometric titration of 0 05M hafnium sulphate solutions with sodium triphosphate solutions of the same concentration showed an inflexion point which corresponds to the ratio $2Hf^{4+}$ $3P_3O_{10}^{5}$ (Fig 1-B) However, the precipitate which was isolated presented a composition which

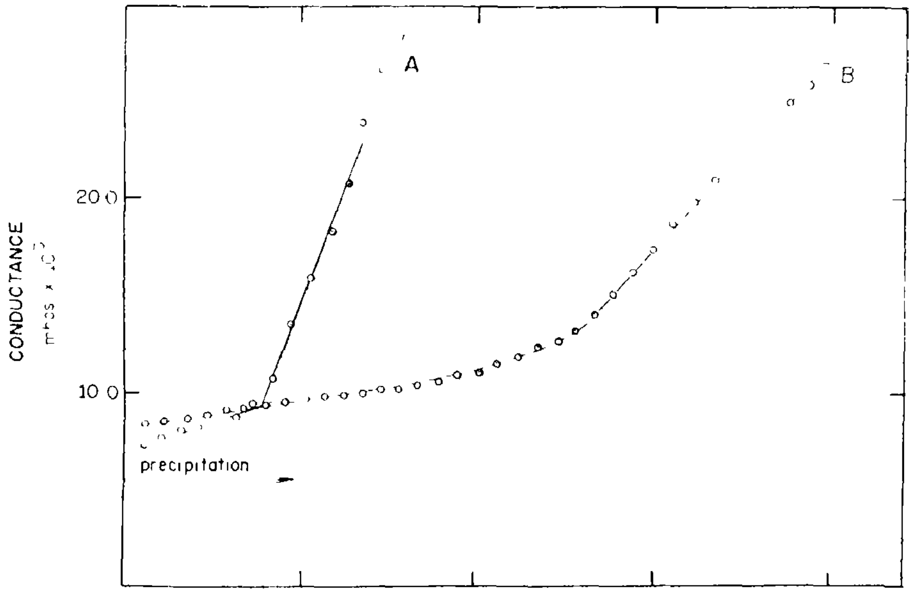


Fig 2 —Conductometric titrations

A—Conductometric titration of 100 ml of 0 005M sodium triphosphate with 0 05M hafnium sulphate

B—Conductometric titration of 100 ml of 0 005M sodium triphosphate with 0 05M hafnyl chloride corresponded to compound II i.e., $2HfO^{2+} : 1P_3O_{10}^{5-}$. This result can be explained by considering the hydrolysis

$$2Hf^{4+} + 2H_2O \rightleftharpoons 2HfO^{2+} + 4H^+,$$

the resulting H^+ ions and the $P_3O_{10}^{5-}$ ions reacted conform

$$2P_3O_{10}^{5-} + 4H^+ \rightleftharpoons 2H_2P_3O_{10}^{3-}$$

So, $2P_3O_{10}^{5-}$ are necessary for the above reaction and one $P_3O_{10}^{5-}$ for the combination with $2HfO^{2+}$, giving the compound II.

(3) The titration of 0.05 M sodium triphosphate solution with 0.05M hafnyl chloride showed the formation of an insoluble compound with the ratio $5HfO^{2+} : 4P_3O_{01}^{5-}$ (Fig. 1-C). This composition corresponds to compound I mentioned above (See p. 893).

(4) The titration of 0.05 M hafnyl chloride with sodium triphosphate of the same concentration showed an inflexion point that corresponds to an insoluble compound with the ratio $2HfO^{2+} : 1P_3O_{10}^{5-}$ (Fig. 1-D). This compound (II) was prepared accordingly to the prodecure indicated in page 894.

B. *Conductometric titrations*

(1) The titration of 0.005 M sodium triphosphate solutions with 0.05 M hafnium sulphate solutions (Fig. 2-A) indicated clearly *an inflexion point corresponding to a ratio* $2Hf^{4+} : 3P_3O_{10}^{5-}$. However, the product obtained in this case was identical to compound II, corresponding to a composition $2HfO^{2+} : 1P_3O_{10}^{5-}$. In the present case, in accordance to the dilution effect, no solubilization occurred, as was observed *in the potentiometric titrations* (see p. 894), since the hydrolysis of Hf^{4+} to HfO^{2+} ion was immediate.

(2) The conductometric titration of 0.005 M sodium triphosphate solution with 0.05 M hafnyl chloride showed a very clear inflexion point that corresponds to an insoluble compound with the ratio $5HfO^{2+} : 2P_3O_{10}$ (Fig. 2-B). This compound (III) was prepared according to the procedure indicated in page 894.

Acknowledgements—The authors wish to thank the Conselho Nacional de Pesquisas (Rio de Janeiro) for financial support.

F. GIESBRECHT
G. VICENTINI
M. PERRIER

Departamento de Química
Faculdade de Filosofia, Ciências e Letras,
Universidade de São Paulo
São Paulo, Brazil

Precipitation of tungstates of silver and lead

(*Received* 15 *December* 1962)

UNDER VARYING conditions silver tungstate, silver paratungstate and silver metatungstate has been obtained by SMITH and BRADBURY,[1] GONZALES[2] and KOHN[3] respectively. The formation of normal tungstate of lead, para tungstate of lead and meta tungstate of lead has been reported by ANTHON,[4] SMITH and BRADBURY,[1] BERZELIUS and LOTZ[5] and SCHEIBLER.[6] Some intermediate tungstates of lead have also been reported.

A solution of sodium tungstate gives alkaline reaction which may be due to partial hydrolysis of the salt

$$Na_2WO_4 + 2H_2O \rightleftharpoons 2NaOH + H_2WO_4$$

---

[1] SMITH and BRADBURY, *Ber.* **24,** 2930 (1891).
[2] GONZALES, *J. Prakt. Chem.* **36,** 44 (1887).
[3] F. KOHN, *Z. Anorg. Chem.* **69,** 247 (1911).
[4] F. ANTHON, *J. Prakt. Chem.* **9,** 361 (1836).
[5] BERZELIUS and LOTZ, *J. Prakt. Chem.* **63,** 214 (1844).
[6] SCHEIBLER, *J. Prakt. Chem.* **80,** 204 (1860).

TABLE 1 —PRECIPITATION OF TUNGSTATES OF SILVER

Millimols of WO_3 present in the solution—2 000

	Millimols of Ag added in solution	Millimols present in the supernatant liquid WO_3	Ag	Millimols present in the precipitate WO_3	Ag	Ratio of WO_3 Ag in the precipitate
I	1 624	1 079	x	0 921	1 624	1 1 8
	2 436	0 675	x	1 325	2 436	1 1 8
	3 248	0 216	x	1 784	3 248	1 1 8
	4 060	x	x	2 000	4 060	1 2 0
	4 872	x	0 856	2 000	4 016	1 2 0
	5 684	x	1 624	2 000	4 060	1 2 0
II	1 624	0 438	x	1 562	1 624	1 1 0
	2 436	x	0 099	2 000	2 337	1 1 2
	3 248	x	0 971	2 000	2 277	1 1 1
	4 060	x	1 356	2 000	2 674	1 1 3
	4 872	x	2 514	2 000	2 358	1 1 2
	5 684	x	3 468	2 000	2 216	1 1 1
III	1 624	0 079	0 059	1 921	1 565	1 0 8
	2 436	x	0 674	2 000	1 862	1 0 9
	3 248	x	1 584	2 000	1 664	1 0 8
	4 060	x	2 475	2 000	1 585	1 0 8
	4 872	x	3 625	2 000	1 237	1 0 6
	5 684	x	4 121	2 000	1 463	1 0 7

[I] deals with the precipitation carried out at pH-9 94

[II] deals with the precipitation carried out at pH-8 00

[III] deals with the precipitation carried out at pH-6 70

It may also hydrolyse as follows

$$12(Na_2O\ WO_3) + 7H_2O \rightleftharpoons 5Na_2O\ 12WO_3 + 14NaOH$$

Again a solution of sodium paratungstate becomes acidic after some time with the formation of normal and metatungstates which may be due to the following changes —

$$5Na_2O\ 12WO_3 + H_2O \rightleftharpoons 3(Na_2O\ WO_3) + 2(Na_2O\ 4WO_3) + H_2WO_4$$

As is clear from the above equations, the composition of sodium tungstate solutions will vary much with the ageing of the solution and hydrogen ion concentration In this paper we have investigated the effect of the hydrogen ion concentration upon the composition of the tungstates of silver and lead precipitated from sodium tungstate solution

Experimental

A R chemicals were used during the investigations 20 ml of sodium tungstate solution was treated with 20 ml of silver nitrate or lead nitrate solutions After thorough mixing the precipitate was separated The clear supernatant liquid was then analysed immediately for the metal (silver or lead) and tungstates ions by the usual volumetric and gravimetric methods Thus the composition of the precipitated was derived The precipitation has been studied at different pH by addition of dilute nitric acid lower pH was obtained Care was taken that tungstic acid did not precipitate on the addition of the dilute nitric acid

These results are presented in the following tables in which the last column gives the ratio of tungstate and silver or lead present in the precipitated tungstates

TABLE 2—PRECIPITATION OF TUNGSTATES OF LEAD

Millimols of WO_3 present in each solution—2 000

	Millimols of Pb added in solution	Millimols present in the supernatant liquid WO_3	Millimols present in the supernatant liquid Pb	Millimols present in the precipitate WO_3	Millimols present in the precipitate Pb	Ratio of WO_3 Pb in the precipitate
I	1 200	0 804	x	1 196	1 200	1 1 00
	1 600	0 380	x	1 620	1 600	1 1 10
	2 000	x	x	2 000	2 000	1 1 00
	2 400	x	0 365	2 000	2 035	1 1 02
	2 800	x	0 706	2 000	2 094	1 1 04
	3 200	x	1 048	2 000	2 152	1 1 07
II	1 200	0 462	x	1 538	1 200	1 0 78
	1 600	x	0 024	2 000	1 576	1 0 78
	2 000	x	0 402	2 000	1 598	1 0 80
	2 400	x	0 738	2 000	1 662	1 0 83
	2 800	x	1 112	2 000	1 688	1 0 87
	3 200	x	1 428	2 000	1 772	1 0 88
III	1 200	x	0 205	2 000	0 995	1 0 50
	1 600	x	0 616	2 000	0 984	1 0 50
	2 000	x	1 144	2 000	0 856	1 0 43
	2 400	x	1 472	2 000	0 928	1 0 46
	2 800	x	1 892	2 000	0 908	1 0 45
	3 200	x	2 392	2 000	0 808	1 0 40
IV	1 200	0 444	0 787	1 556	0 413	1 0 26
	1 600	0 202	1 140	1 798	0 460	1 0 26
	2 000	0 104	1 603	1 896	0 397	1 0 26
	2 400	x	1 854	2 000	0 546	1 0 27
	2 800	x	2 267	2 000	0 533	1 0 27
	3 200	x	2 760	2 000	0 440	1 0 22

[I] deals with precipitation at pH-9 94
[II] deals with precipitation at pH-7 50
[III] deals with precipitation at pH-5 50
[IV] deals with precipitation at pH-2 60

Discussion

With sodium tungstate solution at pH 9 94, the normal tungstate of silver Ag_2O WO_3 is precipitated As the pH of the solution is lowered, some formation of silver paratungstate occurs, until at pH 6 7, the precipitate is silver paratungstate 5 Ag_2O 12WO_3

Table 2 shows, that the tungstates of lead are insoluble even in highly acidic medium For precipitation from sodium tungstate solution pH 9 94, a ratio of WO_3 Pb of 1 1 is obtained corresponding to the composition PbO WO_3 i e , the normal tungstate of lead

At pH 7 50, the WO_3 Pb ratio is far from that required for the normal tungstate We believe that at this stage tetra tungstate of lead 3 PbO 4WO_3, as reported by Lefort, is also precipitated With a deficit of Pb ions in the solutions, the precipitate tends to the lead tetra tungstate composition but the tendency is reversed as the lead concentration increases

At pH 5 50, the ratio of WO_3 Pb is slightly more than that required for pure paratungstate of lead *This may be attributed to the adsorption of lead ions on the precipitate formed* The precipitate is, substantially, lead para tungstate

When the medium is highly acidic (pH-2 60), the precipitate is meta tungstate of lead It is interesting to note that lead and tungstate ions are present in the supernatant liquid even before the addition of an equivalent amount of lead ions. This may be due to the solubility of the precipitate in this medium. Also the variation of the WO_3 : Pb ratio from that of pure meta tungstate may be due to the formation of the double salt $PbO \cdot 4WO_3 \cdot Pb(NO_3)_2 \cdot 10H_2O$. The formation of this double salt has also been reported by ROSENHEIM and KOHN[7].

M. C. MEHRA
K. KANT

Department of Chemistry
M. B. M. Engineering College
University of Jodhpur
Jodhpur

[7] A. ROSENHEIM and F. KOHN, *Z. Anorg. Chem.* 69, 247 (1911).

The polyalkaline earth uranates Sr_2UO_5 and Ca_2UO_5

(*Received* 19 *December* 1962)

IN RECENT publications, IPPOLITOVA *et al*.[1, 2, 3] have reported the preparation of the polyalkaline earth uranate Ca_2UO_5 and the apparent non-existence of the corresponding strontium and barium compounds.

Both the calcium and strontium compounds have been prepared and characterized in our laboratory, where an attempt is being made to elucidate their crystal structures. Attempts to prepare Ba_2UO_5 have proved futile.

Preparation and Analysis

The phases were prepared by the solid state reactions shown below.

$$CaUO_4 + Ca_3UO_6 \xrightarrow[\text{Air}]{975^\circ C} Ca_2UO_5$$

$$SrUO_4^* + Sr_3UO_6 \xrightarrow[\text{Air}]{1000^\circ C} Sr_2UO_5$$

The reactant phases used were known from X-ray evidence to be at least 99 per cent pure.

The progress of the reactions was followed by standard X-ray techniques and after frequent remixing and sintering of the reactants, single phase products were obtained for both phases.

The composition of both phases was established by direct chemical analysis. The usual methods[4] were employed to separate uranium from the alkaline earths. Final determinations were made gravimetrically, uranium as U_3O_8, strontium as $SrSO_4$ and calcium as $CaCO_3$.

Oxygen was not determined but a precise oxidimetric determination[5] of the valency Z of uranium was made on both compounds.

Compound	Z	Ratio MO/UO_3
Ca_2UO_5	5.998 ± 0.001	1.998 ± 0.004
Sr_2UO_5	5.999 ± 0.001	1.996 ± 0.003

* Orthorhombic form of $SrUO_4$.

[1] E. A. IPPOLITOVA, BEREZNIKOVA, LEONIDOV and KOVBA, *Issl. Obl. Khim. Urana, Sb. Statei* 159–65 (1961). *Chem. Abs.* **57** 6854i (1962).

[2] BEREZNIKOVA, IPPOLITOVA, SIMANOV and KOVBA, *Issl. Obl. Khim. Urana, Sb. Statei* 151–3 (1961). *Chem. Abs.* **57** 3064d (1962).

[3] IPPOLITOVA, BEREZNIKOVA, KOSYNKIN, SIMANOV and KOVBA, *Issl. Obl. Khim. Urana, Sb. State* 154–8 (1961). *Chem. Abs.* **57** 3064g (1962).

[4] RODDEN, *Analytical Chemistry of the Manhatten Project*, N.N.E.S. VIII-1 McGraw-Hill, New York p. 32, (1950).

[5] SAWYER, unpublished work.

TABLE 1

Guinier camera CuK$_{\alpha_1\alpha_2}$ = 1.5418 Å

Ca$_2$UO$_5$				Sr$_2$UO$_5$			
h k l	Sin$^2\theta$ 10^4 Calc	Sin$^2\theta$ 10^4 Obs	*I*	*h k l*	Sin$^2\theta$ 10^4 Calc	Sin$^2\theta$ 10^4 Obs	*I*
002	202.4	202.5	s–s	002	187.0	187.0	s–s
011	251.4	251.2	s–s	011	232.8	232.8	s–s
102	402.6			110	286.6	287.5	v v w–s
012	403.2	404.4	v v w–d	$\bar{1}11$	289.3		
111	404.5			012	372.5	372.6	v v w–s
200	423.6	423.1	m–s	102	377.4	377.0	v v w–s
$\bar{2}02$	437.3	438.0	m–s	111	378.4		
$\bar{2}11$	580.7	580.5	v s–s	200	404.0	403.8	m–s
013	656.2	655.5	v s–s	$\bar{2}02$	412.8	413.0	m–s
211	769·3	769.8	s–s	$\bar{2}11$	547.5	548.0	v s–s
$\bar{2}13$	796.9	796.0	m–s	$\bar{1}13$	573.9	573.4	v v v w–s
020	803.2	803.5	w–s	013	606.6	607.5	v s–s
004	809.6	809.8	v w–s	$\bar{1}04$	671.0	672.0	v v w–s
202	814.6	816.0	w–s	211	725.7	726.0	m–s
021	853.8	857.0	m–s	020	743.2	742.5	s–s
$\bar{2}04$	856.0			$\bar{2}13$	743.3		
022	1005.6	1006.0	m–s	004	748.2	748.2	v v w–s
121	1006.9			202	769.2	769.5	m–s
$\bar{3}12$	1073.4	1075.0	v v w–s	$\bar{2}04$	795.8	797.0	m–s
220	1226.8	1229.0	w–s	$\bar{3}02$	828.7	830.0	v v v w–s
$\bar{2}22$	1240.6	1241.0	v w–s	120	844.2	844.0	v v w–d
213	1362.7	1360.0	w–s	$\bar{1}21$	846.4		
$\bar{2}15$	1417.9	1420.0	v w–s	022	930.2	931.0	m–s
015	1465.8	1465.8	w–s	014	934.0	935.0	v v w–s
$\bar{4}02$	1519.6	1520.0	w–s	$\bar{3}12$	1014.5	1015.6	m–s
204	1610.4			122	1120.3	1121.5	v v v w–s
042	1612.8	1616.5	m s–d	$\bar{3}04$	1123.0		
222	1617.8			$\bar{1}23$	1131.3	1129.0	v v v w–s
$\bar{2}24$	1659.2	1660.0	m–s	220	1147.2	1145.0	w–s
$\bar{2}06$	1680.4	1680.5	v w–s	$\bar{2}22$	1156.0	1157.0	v w–s
400	1694.4	1695.0	v v w–s	311	1276.0		
$\bar{4}04$	1749.6	1752.3	v w–s	213	1279.0	1281.5	m–d
$\bar{4}11$	1757.2	1755.0	m–s	221	1283.0		
$\bar{4}13$	1785.8	1786.0	v w–s	$\bar{2}23$	1301.0	1301.0	v v w–s
006	1821.6	1823.0	w–s	$\bar{2}15$	1313.0	1315.0	v w–s
031	1857.8	1857.0	w–s	015	1355.0	1355.0	m–s
				123	1398.0	1396.0	v v w–s
				$\bar{1}24$	1414.2	1411.0	v w–s
				$\bar{4}02$	1447.0	1448.0	s–s
				024	1491.4	1489.5	w–s
				222	1512.4	1512.2	s–s
				$\bar{2}24$	1539.2	1539.0	s–s
				$\bar{2}06$	1552.0	1553.0	v w–s
				$\bar{3}15$	1596.0	1596.0	v w–s
				400	1616.0	1617.0	v w–s
				$\bar{4}04$	1651.0	1653.5	w–s
				320	1652.3		
				$\bar{4}11$	1671.0	1672.0	w–s
				$\bar{3}23$	1672.0		
				006	1683.4	1686.0	m–d
				$\bar{4}13$	1688.0		
				$\bar{1}16$	1703.0	1702.0	v v v w–s
				031	1719.2	1721.0	w–s
				124	1771.0		
				130	1773.0	1773.0	v w–s
				$\bar{1}31$	1775.6		
				321	1833.0		
				223	1836.0	1837.0	v v w–s
				$\bar{4}14$	1837.0		

s–s	Strong–sharp
m–s	Medium–sharp
w–s	Weak–sharp
v w–s	Very weak–sharp
m–d	Medium–diffuse

Structural Work

Small crystals of both phases were obtained after microscopic examination of well sintered pellets. The crystals grow with needle habit, the needle axis was later found to be most commonly the crystallographic *b* axis or less frequently the crystallographic *a* axis.

Preliminary Weissenberg diffraction patterns {*h*0*l*, *h*1*l*, *h*2*l* and 0*kl*} revealed that twinning was very common.

In some cases the size of the second component of the twin was small relative to the first, and it proved possible to sort out the diffraction record into the two single lattices.

The single lattice patterns so obtained showed monoclinic symmetry, and the only systematic absences observed were

0*k*0 for *k* odd

*h*0*l* for *l* odd

The space group is uniquely determined as *P*2*l*/*c* No. 14.

The following unit cell data was computed from powder data [Table 1] obtained with a *Guinier* type focussing camera using monochromatized $CuK_{\alpha_1\alpha_2}$ radiation.

Compound	a Å	b Å	c Å	β	V Å³
Ca_2UO_5	7.914 ± 0.004	5.442 ± 0.003	11.45 ± 0.005	108°48′ ± 3′	466.6
Sr_2UO_5	8.112 ± 0.004	5.656 ± 0.003	11.92 ± 0.006	108°58′ ± 3′	517.0

The densities of Ca_2UO_5 and Sr_2UO_5 as determined by a pyknometric method using carbon tetrachloride as pyknometer fluid, were 5.55 g cm^{-3} and 6.08 g cm^{-3} respectively at 21.5°C.

Experience with other uranates prepared by similar methods showed that densities determined by this simple pyknometric method usually represent approximately 95 per cent of the calculated X-ray density.

For either phase, the cell volume and measured density are compatible with a unit cell containing four M_2UO_5 molecules.

The following data has been calculated for $Z = 4$.

	ρX-ray	μCu	μMo
Ca_2UO_5	5.67 g cm^{-3}	1408 cm^{-1}	543.5 cm^{-1}
Sr_2UO_5	6.34 g cm^{-3}	1360 cm^{-1}	699.0 cm^{-1}

In the case of Sr_2UO_5, the positions of the uranium and strontium atoms were derived from Patterson and Fourier projections along the *b* axis, also from a Fourier projection along the *a* axis.

To reduce the series termination errors introduced by using $CuK_{\alpha_1\alpha_2}$ radiation, the strontium parameters given in Table 2 were obtained from difference synthesis of the type $\overline{F_{obs} - F_c}$.

TABLE 2.—Sr_2UO_5 *P*2*l*/*c* No. 14

Atom	Point position	X	Y	Z
U	2(a)	0	0	0
U	2(b)	½	0	0
Sr	4(e)	0.157	0.028	0.328
Sr	4(e)	0.343	0.477	0.140

Further structural work being carried out on Sr_2UO_5 and the isomorphous compound Ca_2UO_5 will be reported in greater detail at a later date.

Acknowledgement—The author thanks the University of Melbourne for the award of a research grant and is indebted to Dr. S. ANDERSSON and Mrs. M. STERNS for their advice and assistance.

Chemistry Department
University of Melbourne
Victoria, Australia

J. O. SAWYER

A study of transference and solvation phenomena

Comments on the papers of J. O. Wear and E. S. Amis

(*Received* 16 *March* 1963)

AMIS AND his coworkers have recently published six papers(1–6) on the determination by the Hittorf method of the transference numbers of UO_2Cl_2(1), $AgClO_4$(2), LiCl(3), KCl(4), NaCl(5) and HCl(6) in water-ethanol mixtures at 25°C. To these solutions they added some nonelectrolyte such as fructose, raffinose, or (in most cases) α-methyl-D-glucoside to act as an "inert reference substance"; analyses after a run yielded ΔG^F_{sol}, the number of grams of solvent that had moved per faraday relative to this reference substance which was assumed to have remained stationary in the electric field. In pure water or pure ethanol as solvent, the corresponding number of moles of solvent that had moved per faraday (ΔN^F) was given. WEAR and AMIS(7) then employed a computer to determine the solvation numbers of the individual ions in LiCl, NaCl, and KCl solutions from their ΔG^F_{sol} values. As shown below, however, there exists much evidence in the literature that the basic postulate of the method is invalid, and the calculated solvation numbers are therefore devoid of any simple physical meaning.

The idea of adding a reference nonelectrolyte to determine migration of solvent was first proposed by NERNST(8) in 1900, and a summary of the work carried out up to 1939 has been given by MACINNES.(9) In the same year, FISCHER and KOVAL(10) reported that transference numbers in aqueous sulphuric acid changed when various nonelectrolytes (urea, acetone or sucrose) were added to the solutions, and they suggested that part of the reference substance travels with the ions. More conclusive evidence in support of this interpretation appeared after the end of World War II. LONGSWORTH(11), using the more accurate moving boundary technique, found that not only did ΔN^F in aqueous 0.2*M* LiCl solution depend upon the reference substance employed, but even on extrapolation to zero concentration of added nonelectrolyte the results -1.16 for urea and 1.94 for raffinose—differed by over 50 per cent. Greater variations still were discovered by HALE and DE VRIES(12) in their Hittorf experiments with aqueous solutions of tetra-alkylammonium iodides: with 0.1*M* NMe_4I, for example, ΔN^F was four with maltose as reference substance, six with acetone, and twenty with ethyl acetate. Their data was equally well accommodated by the hypothesis that the water was stationary and that each mole of iodide ions was associated with 0.011 mole maltose, 0.029 mole acetone or 0.10 mole of ethyl acetate, respectively. This alternative interpretation of the results is eminently reasonable since the molecules of the reference substances are polar and so interact with and are transported by the ions, and the curious inconstancy of ΔN^F is thereby readily

(1) D. M. MATHEWS, J. O. WEAR, and E. S. AMIS, *J. Inorg. Nucl. Chem.* **13**, 298 (1960).
(2) W. V. CHILDS and E. S. AMIS, *ibid.* **16**, 114 (1960).
(3) J. O. WEAR, C. V. MCNULLY, and E. S. AMIS, *ibid.* **18**, 48 (1961).
(4) J. O. WEAR, C. V. MCNULLY, and E. S. AMIS, *ibid.* **19**, 278 (1961).
(5) J. O. WEAR, C. V. MCNULLY, and E. S. AMIS, *ibid.* **20**, 100 (1961).
(6) J. O. WEAR, J. T. CURTIS JR., and E. S. AMIS, *ibid.* **24**, 93 (1962).
(7) J. O. WEAR and E. S. AMIS, *ibid.* **24**, 903 (1962).
(8) W. NERNST, *Nachr. Kgl. Ges. Wiss. Gottingen*, 68 (1900).
(9) D. A. MACINNES, *The Principles of Electrochemistry*, Reinhold, New York, pp. 91–95 (1939).
(10) P. Z. FISCHER and T. E. KOVAL, *Bull. Sci. Univ. Kiev* no. 4, 137 (1939).
(11) L. G. LONGSWORTH, *J. Amer. Chem. Soc.* **69**, 1288 (1947).
(12) C. H. HALE and T. DE VRIES, *ibid.* **70**, 2473 (1948).

explained The reference substances, then, are no more inert than the solvent itself(13), and the evidence from the above and other experiments(14) shows conclusively the incorrectness of the fundamental assumption that the added nonelectrolyte but not the solvent is stationary in the electric field The ΔN^F and ΔG^F_{sol} values obtained are thus no more than convenient parameters with which to express the experimental results(11), and the so-called solvation numbers calculated from them by WEAR and AMIS(7) do not have the significance that their name implies

M SPIRO

Department of Chemistry
Imperial College of Science and Technology
London S W 7

(13) A R GORDON, *Ann Rev Phys Chem* **1**, 61 (1950)
(14) A HUNYAR, *J Amer Chem Soc* **71**, 3552 (1949)

Diosmium oxyoctachloride*

(*Received* 15 *March* 1963, *in revised form* 1 *April* 1963)

CHLORINATION of osmium at 650-700 is known to give $OsCl_4$ in 50 65 per cent yield along with a small amount of more volatile material described as a mixture of chlorides (1)

When the chlorination was carried out with a 15 to 1 mixture of Cl_2 and air, crystalline Os_2OCl_8 was isolated in 77 per cent yield as well as $OsCl_4$ (10 per cent) Freshly prepared, the oxychloride was soluble in petroleum ether, benzene, and ether, and it was very hygroscopic The infrared spectrum showed a medium band at 10 02 μ (OsO) that disappeared on brief exposure of the sample to moist air

The only true osmium oxychloride previously reported is $OsOCl_4$ prepared by treatment of osmium with an 8 1 ratio of Cl_2 and O_2 at 400 (2) The structure Cl_4Os O—$OsCl_4$ is plausible for the new oxychloride in view of the existence of Os^V in OsF_5(3,4) and of pentacoordinate Os in $OsOCl_4$ and OsO_3F_2 (4) The close similarity in properties between $ReOCl_4$ and $OsOCl_4$(2) suggests that the unknown Re_2OCl_8 may be capable of existence

Attempted sublimation of Os_2OCl_8 at 125 , 5 mm gave a sublimate of $OsCl_3$ Found Cl 35 93, Os, 63 83 Calc for $OsCl_3$ Cl, 35 87, Os, 64 13% The oxychloride deliquesced during the rapid transfer to the nitrogen-filled sublimation tube

$$2\,Os + 4Cl_2 + \tfrac{1}{2}O_2 \xrightarrow[700^\circ]{} Cl_4Os\text{—}O\text{—}OsCl_4$$

$$Cl_4Os\text{—}O\text{—}OsCl_4 \xrightarrow[125^\circ]{5\ mm} OsCl_3 + \text{Residue}$$

Preparation

A 1 m length of 25 mm dia Vycor tubing was heated to 675 700° in a 33 cm furnace The tube was insulated up to 35 cm beyond the furnace and inclined slightly from the horizontal to permit later flow of the product from the hot zone After the tube was flushed with nitrogen 8 0 g of 10 mesh Os sponge was added in a porcelain boat, the tube was flushed with nitrogen and a mixture of Cl_2 and air in a volume ratio of about 15 to 1 was introduced at a rate of 3-4 bubbles sec for 9 hr A red-brown liquid formed and slowly crystallized beyond the furnace The tube was cooled under

---

* This investigation was conducted under U S Air Force Contract AF 33(616)-7214 monitored by the Materials Central Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio

(1) O RUFF and F BORNEMANN, *Z anorg Chem* , **65**, 446 (1910)
(2) M A HEPWORTH and P L ROBINSON *J Inorg Nucl Chem* , **4**, 24 (1957)
(3) G B HARGREAVES and R D PEACOCK, *J Chem Soc* , 2618 (1960)
(4) G H CADY and G B HARGREAVES, *J Chem Soc* , 1568 (1961)

a nitrogen stream, the $OsCl_4$ that had collected immediately beyond the hot zone was removed from the entrance end, and the Os_2OCl_8 removed from the exit end under nitrogen. From 5.51 g of consumed Os was obtained 1.0 g (10 per cent) of $OsCl_4$ and 7.6 g (77 per cent) of Os_2OCl_8. Found: Cl, 41.65, Os, 55.97, O, 2.38 (by difference). Calc. for Os_2OCl_8: Cl, 41.70, Os, 55.92, O, 2.35%. Calc. for $OsOCl_4$: Cl, 40.75, Os, 54.66, O, 4.59%.

Without air in the Cl_2 stream, the preceding procedure yielded 85 per cent $OsCl_4$; no purification(1) was necessary. Found: Cl, 42.67, Os, 56.87. Calc. for $OsCl_4$: Cl, 42.72, Os, 57.28%.

Research Department
Wyandotte Chemicals Corporation
Wyandotte, Michigan

R. L. SCHAAF

J Inorg Nucl Chem, 1963, Vol 25, p 905 Pergamon Press Ltd Printed in Northern Ireland

ERRATUM

A G MASSEY Pentacarbonylacrylonitriletungsten, *J Inorg. Nucl Chem.* **24,** 1172–1174 (1962) Page 1174, table, column 4

for	"C–N Stretch"	read	"C≡N Stretch"
	C≡O Stretch		C=O Stretch
	C=O Stretch		C≡O Stretch
	C–O Stretch		C- -O Stretch
	C≡O Stretch		C=O Stretch
	C=C Stretch		C≡C Stretch

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 907 to 918. Pergamon Press Ltd. Printed in Northern Ireland

BROMINE EXCHANGE IN GRAPHITE-BROMINE LAMELLAR COMPOUNDS*

S. ARONSON
Brookhaven National Laboratory, Upton, New York

(*Received* 21 *January* 1963, *in revised form* 20 *February* 1963)

Abstract—A kinetic study of the exchange of normal and radioactive bromine in graphite-bromine lamellar compounds has been made at temperatures of 30° to 50°C. Natural and synthetic powders were investigated. Two alternative mechanisms for the exchange, volume diffusion and surface exchange, were considered. The data were in better agreement with the diffusion mechanism. Diffusion coefficients of 10^{-9}–10^{-8} cm²/sec and an activation energy of 11–14 kcal/mole were calculated for the natural graphite powders. The diffusion coefficients increased with increasing bromine content. Reversibly absorbed bromine exchanged more rapidly than irreversibly absorbed bromine.

BROMINE is one of a group of substances which is able to penetrate between the planes of the graphite structure to form lamellar compounds.(1–3) A continuous range of graphite-bromide compositions up to a limiting composition of C_8Br is formed. It is difficult to determine to what extent solid solution regions exist and to what extent compounds of definite stoichiometry occur. MAIRE and MERING(4) have concluded, on the basis of X-ray and vapour-pressure data, that two types of bromine layers occur, Type I and Type II. Below a composition of approximately $C_{16}Br$, bromine penetrates only between some of the graphite planes to form bromine layers of Type I. These layers have two-dimensional crystallographic order. At the composition $C_{16}Br$, there is a bromine layer for every two carbon layers and the structure has achieved three-dimensional order. Above a composition of $C_{16}Br$, additional bromine is added to some of the bromine layers to form layers of Type II. At a composition of C_8Br, all the layers are of Type II.

It is evident from this unusual picture of compound formation that the graphite-bromine system is complex. The complexity of the system is further illustrated by the facts that the added bromine is only partially ionized, a hysteresis loop is observed in moving through a bromine vapour-pressure cycle, and only part of the bromine can be reversibly removed and readsorbed by changes in vapour-pressure.(1–3)

HOOLEY(5) has studied the rates and extent of bromination of natural graphites of various particle sizes. The amount of bromine absorbed was found to be dependent on the particle size of the graphite. Large crystals (1 to 2 mm) formed the composition

---

*This work was performed under the auspices of the United States Atomic Energy Commission.

(1) G. R. HENNIG, *Interstitial Compounds of Graphite, Progress in Inorganic Chemistry*, Vol. 1 (Edited by F. Albert Cotton), Interscience, New York (1959).

(2) W. RÜDORFF, *Graphite Intercalation Compounds, Advances in Inorganic Chemistry and Nuclear Chemistry*, Vol. 1 (Edited by H. J. Emeleus and A. G. Sharpe), Academic Press, New York (1959).

(3) A. R. UBBELOHDE and F. A. LEWIS, *Graphite and Its Crystal Compounds*, Clarendon Press, Oxford (1960).

(4) J. MAIRE and J. MERING, *Proceedings of the Third Conference on Carbon* p. 337. Pergamon Press, London (1959).

(5) J. G. HOOLEY, *Canad. J. Chem.* **40**, 745 (1962).

C_8Br over a wide range of partial pressures The bromine content of small crystals increased with increasing partial pressure Hooley measured rates of bromination at temperatures of −12°–20°C The initial rates were inversely proportional to bromine content with an activation energy of 2 4 kcal/mole

The purpose of the present study was to obtain information on the mobility of bromine in graphite–bromine compounds Rates of exchange of normal and radioactive bromine in graphite-bromine powders have been investigated between 30° and 50°C Possible mechanisms for the exchange are discussed and the effects of temperature, particle size, and bromine content are considered

EXPERIMENTAL

Materials

Two types of pure graphite powder (10 p p m impurities) obtained from the National Carbon Company were used , a natural graphite powder, SP1 spectroscopic graphite, and an artificial graphite powder, SP2 spectroscopic graphite They were fractionated by sieving The fraction of SP1 powder which passed through a 400 mesh screen (37 μ) was designated SP1-37 The sieve fraction between 200 and 150 mesh (74-105 μ) was designated SP1-74 The sieve fraction of SP2 powder between 100 and 80 mesh (149–177 μ) was called SP2-149 The surface areas of the SP1-37, SP1-74, and SP2-149 powders, determined by nitrogen adsorption, were 2 3 1 6, and 1 3 m^2/g respectively The densities, obtained by helium displacement measurements, were 2 30 ± 0 04, 2 27 ± 0 02, and 2 14 ± 0 02 g/cm^3 respectively The interlayer spacings were determined by X-ray diffraction to be 3 357 ± 0 002 Å, 3 356 ± 0 002 Å, and 3 364 ± 0 002 Å respectively for the SP1-37, SP1-74, and SP2-149 powders The higher densities and smaller interlayer spacings of the SP1 powders reflect the greater crystalline perfection of the natural powders as compared to the artificial powder

Reagent grade bromide was procured from the Fisher Scientific Co A middle fraction of the liquid was obtained by distillation in vacuo and was utilized in the experiments

Microscopic observations

The three powders were observed under the optical microscope Small portions of the powder were dusted onto microscope slides and were observed at magnifications up to 500 The SP2-149 particles were generally oval in shape with diameters ranging between 140 and 190 μ The SP1-37 powder exhibited a wide variety of sizes and shapes and surface structures The smallest dimensions of the particles were between 10 and 50 μ The smallest dimensions of the majority of the particles were between 15 and 35 μ The SP1-74 powder consisted of particles whose smallest dimensions were between 50 and 130 microns The majority of the particles had dimensions between 60 and 110 μ

The range of particle sizes observed microscopically for each of the powders was somewhat wider than that estimated from the sieve sizes used The discrepancy may be due to nonuniform openings in the sieves and to inaccuracies in estimating particle sizes from microscopic observations on irregularly shaped particles

Experimental procedures

Formation of graphite–bromine compounds The experimental conditions required to form graphite bromine compounds of various compositions were determined with the aid of a quartz spring balance * It had a sensitivity of 1 44 mg/mm A graphite sample weighing about 0 1 g was placed in a quartz pan and attached to the spring The sample chamber was evacuated to 10^{-3} mm Hg The sample temperature was controlled to +0 1°C by use of a water bath or a large Dewar vessel Tubes containing liquid bromine were connected to the system, evacuated and thermostatted separately The bromine was allowed to enter the sample tube and weight changes were recorded The pressure of bromine was calculated from the temperature of the bromine liquid using the equation of FISCHER (6)

$$\log P = 2199\ 0/T - 4\ 150 \log T + 19\ 9618 \qquad (1)$$

The pressure P is in mm Hg T is in degrees Kelvin

---

*The spring was obtained from the Microchemical Specialties Co , Berkeley, California

(6) J FISCHER and J BINGLE, *J Amer Chem Soc* 77, 6511 (1955)

Bromine exchange The bromine exchange experiments were performed in the apparatus shown in Fig 1 A weighed amount (0 1–0 4 g) of graphite powder was placed on the sintered quartz disk in the "U" tube The sample was evacuated and exposed to radioactive bromine After sufficient time was allowed for the complete formation of the graphite-bromine compound (above 2 hr), the "U" tube was closed off The rest of the system was evacuated for 30 min to remove radioactive bromine from the silicone grease used in stopcocks and joints Normal bromine was then passed through the sample at the brominating pressure and was collected by condensation in one of the collection tubes immersed in an ice-bath In some cases, the radioactivity of the collected bromine sample was measured directly by placing the collection tube in a γ-counter In other cases, the bromine was dissolved in a basic solution of sodium thiosulphate and an aliquot was taken After a number of bromine samples were collected, the "U" tube was shut off from the bromine reservoir The removable bromine remaining in the graphite sample was drawn into a collection tube for one hour by condensation in liquid nitrogen This final sample of bromine and the graphite sample itself were then counted Corrections were made on all the samples for radioactive bromine trapped in the grease and in the unoccupied volume of the "U" tube by making blank runs in the absence of graphite

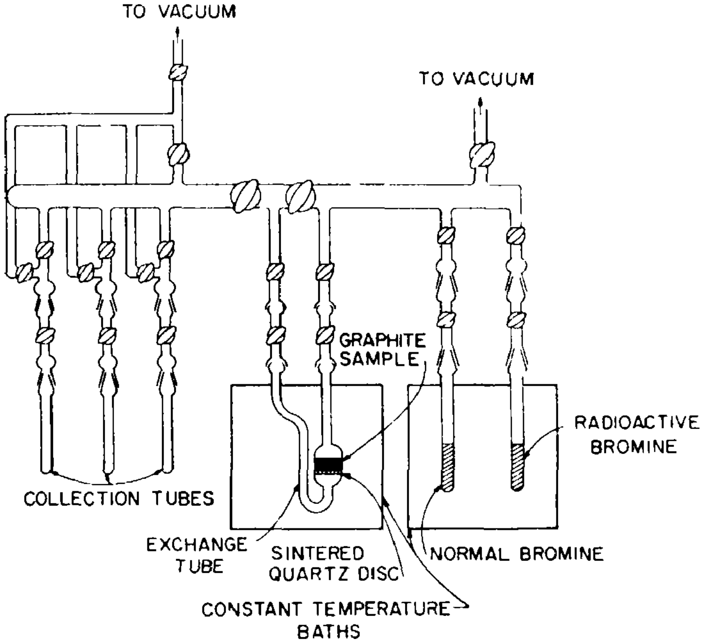


FIG 1 —*Bromine exchange system*

The radioactive bromine samples were obtained by exposing normal bromine to a thermal neutron flux of approximately 10^{13} neutron cm/sec for several minutes in the Brookhaven Graphite Research Reactor The only relatively long-lived isotope formed, bromine-82, has a half-life of 35 7 hr

The validity of the exchange procedure was established by obtaining data on powder samples of various weights The data obtained from exchange runs were used only if similar results were obtained for different weights of sample

Experiments in which the temperature of the bromine reservoir was above room temperature were performed with the whole system surrounded by a plastic enclosure The air within the enclosure was heated to above the temperature of the bromine

KINETIC EQUATIONS

The physical model that is used for each of the graphite powders is that of a group of right circular cylinders of varying diameter It is assumed that the particles have a uniform weight distribution throughout the range of particle sizes. The graphite planes are assumed to lie perpendicular to the edges of the cylinders. Bromine exchange between the solid and the gas occurs only at the edges. Although this model is highly idealized, it has a qualitative resemblance to the real systems. It is useful in correlating the experimental data and in obtaining semiquantitative kinetic information.

Two possible rate controlling processes for the istopic exchange of bromine in graphite are the self-diffusion of bromine in the graphite and the exchange between adsorbed and gaseous bromine at the surface of the graphite. For uniform cylindrical particles, the diffusion equation is, in the case of a constant surface concentration,[7]

$$\alpha' = 1 - \sum_{n=1}^{\infty} (4/K_n^2) \exp(-DtK_n^2/a^2) \tag{2}$$

α' is the fractional degree of completion of the exchange and varies from a value of zero to one. D is the diffusion coefficient and t is the time. The symbol, a, refers to the particle radius. The K_n constants are zeros of the Bessel function of the first kind of order zero.

A general kinetic equation for a distribution of particle sizes, $F(a)$, is

$$\alpha(t) = \int_{a_1}^{a_2} \alpha'(t, a)F(a)\,da \bigg/ \int_{a_1}^{a_2} F(a)\,da \tag{3}$$

a_1 and a_2 are the maximum and minimum particle radii in the distribution. The distribution function, $F(a)$, is assumed to be a constant. Inserting Equation (2) into Equation (3) and integrating, one obtains the equation

$$\alpha = 1 - (1/R - 1)\sum_{n=1}^{\infty} [4/K_n^2 \{R \exp -(K_n\tau_1/R)^2 - \exp -(K_n\tau_1)^2\} \\ - 4\pi^{1/2} \tau_1/K_n \{\mathrm{erf}(K_n\tau_1) - \mathrm{erf}(K_n\tau_1/R)\}] \tag{4}$$

Erf $(K_n\tau_1)$ is the error function of $K_n\tau_1$. τ_1 is defined as the parameter $(Dt)^{1/2}/a_1$. R is the ratio a_2/a_1.

A comparison of the curves obtained for R values of 1 and 3 in Equation (4) is shown in Fig. 2. The rate of exchange falls off more rapidly with time for the larger value of R.

The alternative mechanism, that the rate of exchange between adsorbed and gaseous bromine at the surface is rate controlling, is now considered. The radioactive bromine removed from the solid is assumed to be continuously swept away so that the gas phase consists only of normal bromine. The first-order kinetic equation for uniform particles is

$$\alpha = 1 - \exp(-kt/a) \tag{5}$$

k is a first-order rate constant. The rate of exchange is inversely proportional to the surface to volume ratio of the particle and, hence, to $1/a$. Inserting Equation (5) into Equation (3) and integrating, we obtain the equation for a range of particle sizes

$$\alpha = 1 - (1/R - 1)[R \exp(-\tau_2/R) - \exp(-\tau_2) + \tau_2\{E(\tau_2) - E(\tau_2/R) - \ln R\}] \tag{6}$$

---

[7] J. CRANK, *The Mathematics of Diffusion*, Chap. 5, Clarendon Press, Oxford (1956).

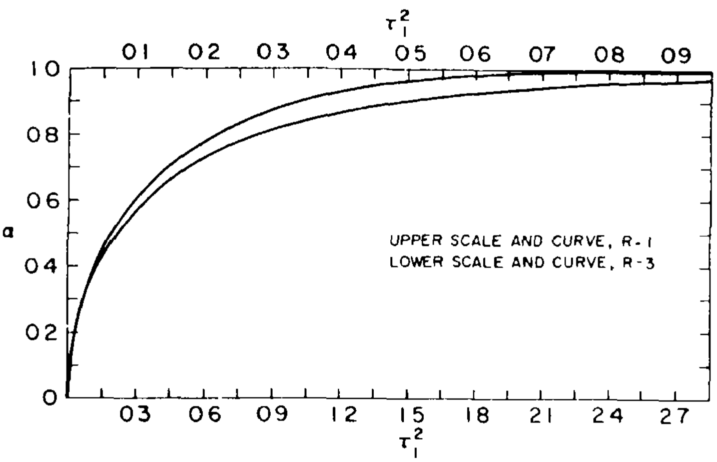


FIG. 2.—Comparison of Equation (4) for R values of 1 and 3.

τ_2 is the parameter kt/a_1. $E(\tau_2)$ is an exponential-integral function of τ_2, i.e., $\int_0^{\tau_2}(1 - e^{-x}/x)\,dx$. Values for the exponential-integral function can be obtained from Tables[8].

A comparison of the rate curves obtained from Equations (4) and (6) is shown in Fig. 3 for a value of $R = 2$. It is observed that the diffusion curve falls off more rapidly with time than does the surface exchange curve.

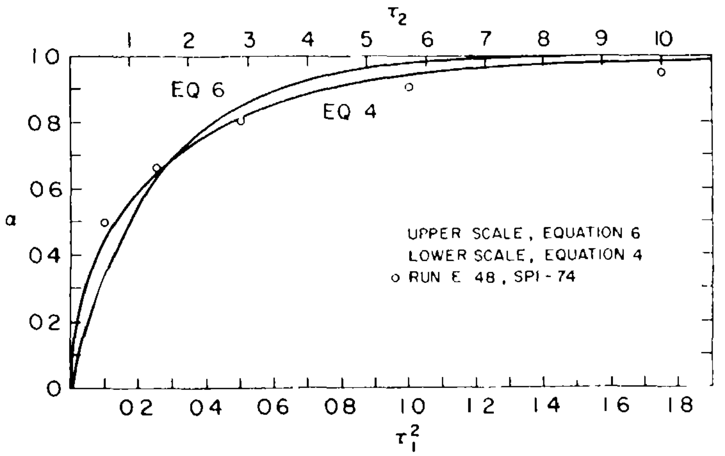


FIG. 3.—Comparison of Equations (4) and (6) for an R value of 2.

RESULTS AND DISCUSSION

The experimental conditions under which the bromine exchange runs were performed are summarized in Table 1. The graphite-bromine compositions studied were chosen to be in the range between the pure Type I compound ($C_{16}Br$) and the pure Type II compound (C_8Br) discussed by MAIRE and MERING[4]. Bromine compositions close to C_8Br were not studied to avoid the problems of capillary condensation

---

[8] *Tables of the Generalized Exponential Integral Functions*, Harvard University Press, Cambridge (1949).

TABLE 1 INFORMATION ON THE BROMINE EXCHANGE EXPERIMENTS

Run no	Type of graphite	Br/C atomic ratio	Graphite tempera-ture (°C)	Bromine pressure* (mm Hg)	Relative pressure† P/P_0	Ratio of bromine, residue/lamellar
E-23	SP2-149	0 049	30 0	125	0 49	0 24
E-43	SP2-149	0 049	30 0	125	0 49	0 23
E-39	SP2-149	0 049	38 0	191	0 54	0 24
E-40	SP2 149	0 049	38 0	191	0 54	0 24
E-46	SP2-149	0 049	48 0	342	0 66	0 24
E-36	SP2-149	0 049	48 0	342	0 66	0 23
E-22	SP2-149	0 067	30 0	191	0 74	0 21
E-50	SP2-149	0 066	38 0	297	0 84	0 23
E-51‡	SP2-149	0 064	38 0	191	0 54	0 24
E-44	SP1-37	0 082	30 0	125	0 49	0 18
E-25	SP1-37	0 082	30 0	125	0 49	0 16
E-32	SP1-37	0 082	38 0	191	0 54	0 17
E-41	SP1-37	0 082	38 0	191	0 54	0 17
E-37	SP1-37	0 082	48 0	342	0 66	0 15
E-45	SP1-37	0 103	30 0	191	0 74	0 15
E-52	SP1-37	0 100	38 0	297	0 84	0 16
E-60‡	SP1-37	0 100	38 0	191	0 54	-
E-56	SP1-74	0 085	30 0	125	0 49	0 27
E-48	SP1-74	0 085	38 0	191	0 54	0 28
E-57	SP1-74	0 085	48 0	342	0 66	0 26
E-53	SP1-74	0 108	38 0	297	0 84	0 25
E-59‡	SP1-74	0 104	38 0	191	0 54	-

* Pressures were calculated from the temperature of the bromine reservoir using Equation (1)

† The relative pressure is the ratio of the bromine pressure over the graphite to the vapour pressure of liquid bromine at the temperature of the graphite

‡ In these experiments, the samples were prepared at a relative pressure of 0 84 The relative pressure was lowered to 0 54 before each exchange run

and extensive surface adsorption It is observed in Table 1 that the natural graphite powders contain almost twice as much bromine as the artifical powder under equivalent conditions This agrees with the results of MAIRE and MERING[(4)] who attributed the greater uptake of bromine in natural graphite to the more nearly perfect lattice structure The work of HOOLEY[(5)] indicates that the amount of bromine absorbed by graphite may also be a function of particle and crystallite size This may account for the small differences in bromine content between SPI-37 and SPI-74 powders

The final step in each exchange run was to connect the sample chamber to a liquid nitrogen trap for 1 hr to remove the reversibly absorbed bromine The fraction of bromine which could not be removed by evacuation, forming the so-called "residue compound", is shown in the final column of Table 1

Within the range of experimental conditions employed, the rate data were independent of the flow rate of the bromine gas and the weight of the graphite sample It was necessary to maintain the space surrounding the graphite sample almost free of radioactive bromine in order to approximate the boundary condition employed in Equations (4) and (6) The flow rate of the normal bromine was kept sufficiently high so that its rate of condensation in the collection tube was at least twenty times as high as the rate of collection of radioactive bromine from the graphite sample

The rate data obtained in the exchange runs are summarized in Table 2. Several exchange runs are plotted in Fig. 4. The rate data were compared to the two mechanisms discussed in the previous section. Much better agreement was obtained with the diffusion mechanism than with the surface exchange mechanism. However, some systematic deviation was observed from the diffusion model. It was, therefore, decided to first make an internal comparison of the data for each powder. The comparison was based on the assumption that the kinetic curves for each powder are independent of temperature and composition if the time parameter is modified by the proper proportionality constant. Equations (4) and (6) are examples of such an assumption. Curves E-23, E-43 for SP2-149, E-25, E-44 for SP1-37, and E-56 for SP1-74 were considered as "standard" curves to which the rest of the data could be compared. The time required to reach a specified fractional completion at temperature was compared to the time required to reach the same fractional completion at 30°C. Some of these plots are shown in Figs. 5 and 6. The linear nature of the curves indicates that a single kinetic mechanism can account for the data for each powder at the different temperatures. The relative rate constants, calculated from the slopes of the lines in Figs. 5 and 6 and from some additional data are shown in Table 2. The results indicate that the three powders behave kinetically in a similar manner. It is observed that the rate constant increases with temperature and with bromine content. In runs E-51, E-60, and E-59, the pressure of bromine was lowered

TABLE 2.—RATE DATA IN THE BROMINE EXCHANGE EXPERIMENTS

Run no.	Type of graphite	Br/C atomic ratio	Temperature (°C)	Relative rate constant	Diffusion coefficient (cm²/sec × 10⁹)	Activation energy (kcal/mole)
E-23	SP2-149	0.049	30.0	1		12
E-43	SP2-149	0.049	30.0			
E-39	SP2-149	0.049	38.0	1.6		
E-40	SP2-149	0.049	38.0	1.6		
E-46	SP2-149	0.049	48.0	3.2		
E-36	SP2-149	0.049	48.0	3.3		
E-22	SP2-149	0.067	30.0	1.6		
E-50	SP2-149	0.066	38.0	2.6		
E-51	SP2-149	0.064	38.0	2.7		
E-44	SP1-37	0.082	30.0	1	3.0	14
E-25	SP1-37	0.082	30.0			
E-32	SP1-37	0.082	38.0	1.7	5.1	
E-41	SP1-37	0.082	38.0	1.8	5.4	
E-37	SP1-37	0.082	48.0	3.8	11.4	
E-45	SP1-37	0.103	30.0	1.5	4.5	
E-52	SP1-37	0.100	38.0	3.0	9.0	
E-60	SP1-37	0.100	38.0	2.8	8.4	
E-56	SP1-74	0.085	30.0	1	4.3	11
E-48	SP1-74	0.085	38.0	1.7	7.3	
E-57	SP1-74	0.085	48.0	2.9	12.5	
E-53	SP1-74	0.108	38.0	3.1	13.3	
E-59	SP1-74	0.104	38.0	2.8	12.0	

rom 297 to 191 mm Hg prior to the exchange This change in pressure had little ffect on the composition of the solid This is an example of the hysteresis phe-omenon observed(11) in graphite bromine compounds The rate of exchange was lso approximately independent of the pressure

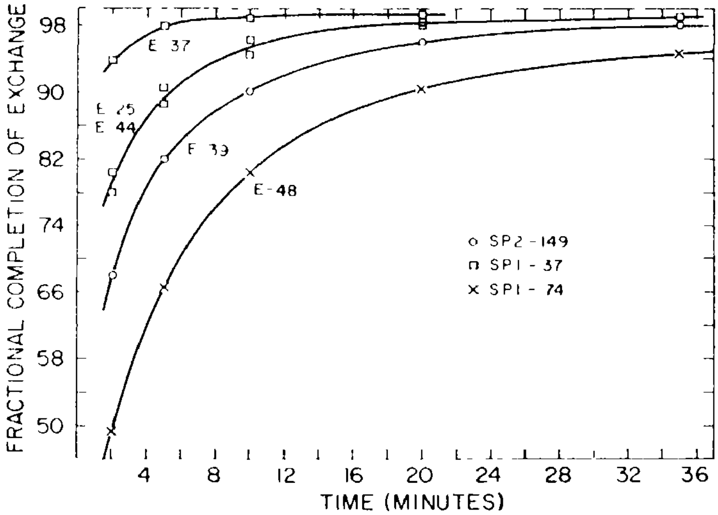


FIG. 4 Rates of bromine exchange

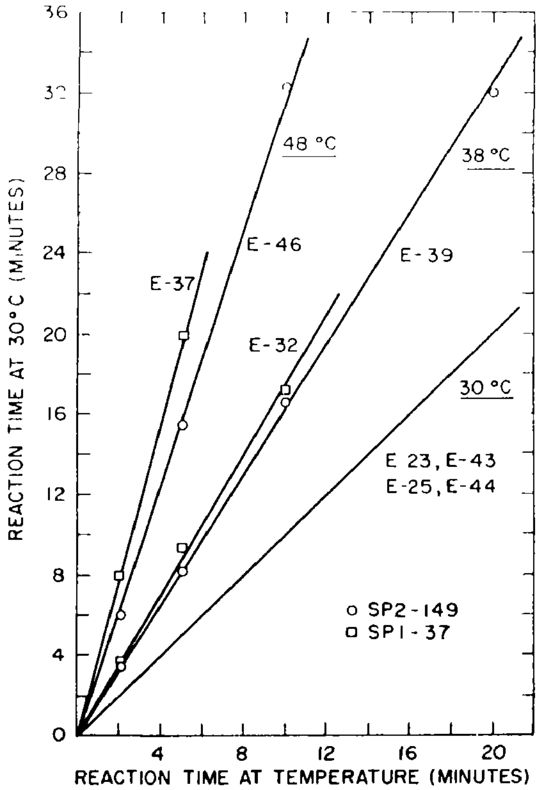


FIG. 5 —Relative rates of bromine exchange for SP1-37 and SP2-149 powders

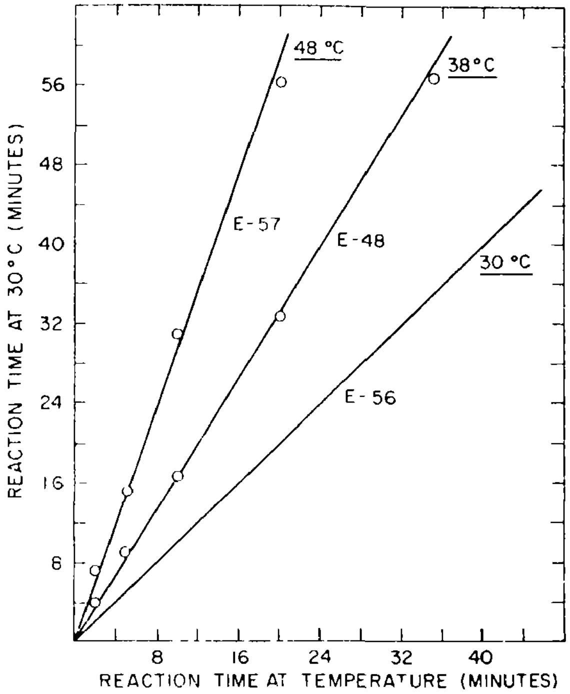


FIG. 6 —Relative rates of bromine exchange for SP1-74 powder

The rate data were compared with Equations (4) and (6) It was previously observe that the particle sizes in the SP1-37 powder ranged from 10 to 50 μ with the majority of them between 15 and 35 μ The SP1-74 powder particles ranged from 50 to 130 μ Most of the particles were between 60 and 110 μ It is likely that the natural graphite powders were approximately in the form of flat plates and were viewed parallel to their thin edges This conclusion is supported by the fact that the surface areas (2 3 and 1 6 m^2/g) are much too large for particles of approximately spherical geometry Furthermore, the difference in surface area between the SP1-37 and the SP1-74 graphites is small The particles in the two powders are probably approximately equal in thickness Most of the surface area is perpendicular to the thin edges through which the reaction is assumed to proceed Most of the surface is, therefore, inactive in the exchange For convenience, the grain structure within the particles was ignored

The physical model which was taken for the natural powders was one of right circular cylinders with a uniform weight distribution from 15 to 45 μ for the SP1-37 powder and from 60 to 120 microns for the SP1-74 powder A uniform distribution of particle weights was assumed for convenience It was felt that a description of each powder in terms of a range of particle sizes would be more accurate than a description involving an average particle size However, because of the variety of sizes, shapes, and surface structures observed in the powders and because of a lack of knowledge of the edge thickness of the particles, it was deemed inadvisable to attempt a careful statistical count of the particles The assumption of a uniform weight distribution was found to be amenable to a relatively simple kinetic treatment and was, therefore, used No attempt was made to estimate a range of particle sizes for the artificial powder, SP2-149. The particles probably do not approximate flat plates.

A comparison of one of the experimental curves shown in Fig. 4 with theoretical curves calculated from Equations (4) and (6) is shown in Fig. 3. The time axis of the experimental curve has been adjusted to meet the theoretical curves at fractional completions of zero and 0.70. For a fractional completion of 0.70, the reaction time of 6 min in Run E-48 corresponds to a value for τ_1^2 of 0.3 and a value for τ_2 of 1.7. τ_1^2 and τ_2 are directly proportional to the reaction time on the basis of Equations (4) and (6). The data are in much better agreement with the diffusion equation, Equation (4), than with the surface exchange equation, Equation (6). The rest of the data on SP1-74 and SP1-37 powders showed similar agreement with the theoretical curves. This comparison with the theoretical curves and the lack of any pressure dependence of the exchange rate indicate that the rates of exchange are governed by a bulk diffusion process. The deviations from the theoretical diffusion curves can be attributed to particle size and shape effects and to the fact that the particles are not single crystals and have some internal grain structure.

Diffusion coefficients were calculated for the natural powders by comparison of the data with the theoretical diffusion curves. *R* values of 2 and 3 were used in Equation (6) for comparison with the SP1-74 and SP1-37 data respectively. The calculated diffusion coefficients are shown in Table 2. The agreement between the two powders is reasonably good. The data is not sufficiently accurate to warrant a discussion of the differences observed between the two powders. The activation energies calculated from the temperature dependence of the exchange were in the range of 11-14 kcal/mole. Only a limited temperature range, 30°–48°C, was employed in this study because of experimental difficulties in using the exchange technique at higher and lower temperatures.

A comparison of bromine exchange in the reversibly absorbed and irreversibly absorbed bromine is shown in Table 3. The fractional completion data for the reversibly absorbed and irreversibly absorbed bromine were obtained after drawing the bromine into a liquid nitrogen trap for one hour and counting the collected bromine and the graphite "residue compound." The exchange in the irreversibly absorbed bromine was less than in the reversibly absorbed bromine in each case. This may indicate that exchange is less rapid in certain regions of each particle than in other regions because of structural differences. On the other hand, the regions containing the irreversibly absorbed bromine may be near the centre of the particles as is suggested by HOOLEY(5). In this case, one would expect less exchange in these regions because of smaller concentration gradients. The effect of the irreversibly absorbed bromine on the exchange kinetics requires further investigation.

It was observed above that a decrease in the bromine pressure had little effect on the bromine content of the solid or on the rates of exchange. Since bromine exchange and the decomposition of graphite–bromine compounds *in vacuo** are rapid, it seems evident that the bromine is not impeded kinetically from leaving the solid when the pressure is lowered. The graphite–bromine composition is probably thermodynamically stable over this range of pressures. The reason that a lower composition is obtained if one adds bromine to graphite at the lower pressure is obscure, however.

*Unpublished data.

TABLE 3.—COMPARISON OF BROMINE EXCHANGE IN REVERSIBLY ABSORBED AND IRREVERSIBLY ABSORBED BROMINE

Run no	Graphite type	Br/C atomic ratio	Graphite temperature (°C)	Reaction time (min)	Total fractional exchange	Fractional exchange in reversibly absorbed bromine	Fractional exchange in irreversibly absorbed bromine
E-27	SP2-149	0.049	30.0	2	0.60	0.65	0.43
E-23	SP2-149	0.049	30.0	35	0.96	0.98	0.91
E-40	SP2-149	0.049	38.0	5	0.83	0.88	0.67
E-39	SP2-149	0.049	38.0	35	0.98	0.99	0.95
E-46	SP2-149	0.049	48.0	20	0.99	0.995	0.96
E-26	SP1-37	0.082	30.0	2	0.80	0.84	0.63
E-44	SP1-37	0.082	30.0	35	0.98	0.99	0.93
E-42	SP1-37	0.082	38.0	5	0.96	0.98	0.87
E-32	SP1-37	0.082	38.0	35	0.99	0.995	0.95
E-56	SP1-74	0.085	30.0	60	0.94	0.97	0.87
E-57	SP1-74	0.085	48.0	35	0.97	0.99	0.91

For kinetic reasons, bromine is, apparently, unable to penetrate into some of the regions in the graphite particles. The primary difference between the two compositions studied in each powder appears to involve the fraction of each particle that is brominated rather than the concentration of bromine in the interlayer spaces. The higher rates of exchange observed for the graphite–bromine compounds of greater bromine content may be due to an increased number of diffusion paths to the surface resulting from the opening up of new regions to the bromine.

The work of HOOLEY(5) indicates that the bromination of graphite results in a fixed composition of C_8Br above a P/P_0 value of 0.5. However, the idea of a constant concentration of bromine in the interlayer spaces over a range of pressure is not in accord with the conclusions of MAIRE and MERING(4) drawn from X-ray diffraction studies.

The activation energies of 11–14 kcal/mole observed for the diffusion of bromine in graphite–bromine are higher than activation energies observed for various kinetic processes involving the interlayer spaces in graphite. Activation energies of 2–3 kcal/mole have been observed for the bromination of graphite,(5) the formation of graphite–ferric chloride compounds,(9) and the diffusion of xenon(10) and, interstitial carbon atoms(11) in graphite. In the case of bromine diffusion the interaction among the bromine molecules themselves is probably more important than the interaction between the bromine and the graphite planes. The space allowed for the bromine between the carbon planes, 3.70 Å,(1–3) is probably sufficiently large to permit easy movement of bromine in the interlayer spaces. The density of bromine between the planes is fairly high, however. A density of 3.42 g/cm^3 has been calculated(1) for the bromine layers in C_8Br compared to densities of 3.12 and 3.4 g/cm^3 for liquid and solid bromine.

---

(9) J. A. BARKER and R. C. CROFT, *Austral. J. Chem.* **6**, 302 (1953).
(10) T. NAKAI, S. YAJIMA, K. SHIBA, J. OSUGI and D. SHINODA, *Chem. Soc. Japan* **33**, 497 (1960).
(11) D. G. SCHWEITZER, *Phys. Rev.* **128**, 556 (1962).

Acknowledgments—The author wishes to acknowledge the able assistance of J G Davis in carr out the experimental work Much useful information on the design of a bromine exchange tube on the preparation of bromine samples for neutron irradiation was obtained from A B Ausk Discussion of this work with Dr D Gurinsky was very helpful The aid of J Sadofsky in obtai information on the lattice parameters and particle sizes of the graphites used is grate acknowledged

J Inorg Nucl Chem, 1963, Vol 25 pp 919 to 921 Pergamon Press Ltd Printed in Northern Ireland

A STUDY OF THE SODIUM RESIDUE FROM A DILUTE SOLUTION OF SODIUM IN LIQUID AMMONIA

I. WARSHAWSKY
Lewis Research Center, National Aeronautics and Space Administration,
Cleveland, Ohio

(*Received* 7 *December* 1962, *in revised form* 5 *February* 1963)

Abstract—Dilute solutions of sodium in liquid ammonia at −78°C were prepared in quartz ampules Previous work has shown that such solutions react with strongly adsorbed water on the container surface After allowing the solution to react, the ammonia was pumped off The residue evolved hydrogen when heated in vacuum This suggests that the residue contained sodium hydride Hence, not all the hydrogen formed in the reaction is evolved from the blue solution, but some remains behind chemically combined with sodium

THE wide use of Pyrex and quartz containers in the study of dilute solutions of alkali metals in liquid ammonia makes it desirable to understand the effect that a glass surface has on the stability of the metal-ammonia system In a previous paper(1) evidence was presented which suggests that the initial instability of a dilute solution of sodium in liquid ammonia at −78°C is due to a reaction between strongly adsorbed water on the Pyrex surface and the metal ammonia solution in which hydrogen gas is evolved The present investigation is concerned with the question of whether all the hydrogen is evolved as hydrogen gas or some remains behind in the blue solution forming an intermediate species such as hydride With this in mind, the residue from a dilute solution of sodium in liquid ammonia is tested for a possible source of hydrogen under defined experimental conditions

EXPERIMENTAL

A simple procedure for testing the sodium residue for a source of hydrogen is heating the residue from a dilute solution of sodium in liquid ammonia under defined conditions and observing how much gas is evolved

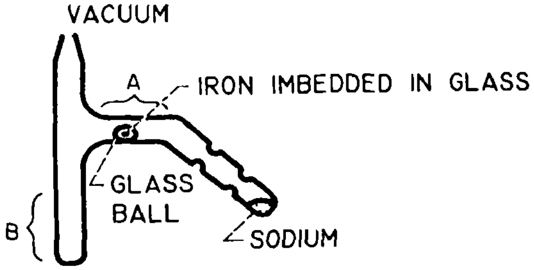


FIG 1 Study of glass surface at Region *B*

Test for presence of adsorbed water on container surface

A technique for transferring small quantities of sodium (10^{-6} moles) under "stick" vacuum conditions (less than 10^{-6} mm Hg) has been previously described (1) Briefly, this technique consisted of distilling sodium onto the surface of a glass ball containing a small piece of iron imbedded in it By means of a magnet the coated ball was transferred from region *A* to *B* (Fig 1), and the sodium was distilled from the glass ball surface onto the wall of region *B* Evolution of hydrogen was taken as evidence for a reaction between the sodium and water adsorbed on the glass surface

---

(1) I WARSHAWSKY, *J Inorg Nucl Chem* 25, 601 (1963)

Since it could be baked at higher temperatures than a Pyrex ampule, a quartz ampule was used in the present experimental work The results obtained in baking region *B* under "stick" vacuum conditions are summarized below

TABLE I

Treatment of quartz ball (C)	Treatment surface *B* (C)	Time (hr)	Pressure of gas evolved (μ)
600	600	20	0 35 ± 0 03
830	830	20	0 35 ± 0 03
830	830	80	0 35 ± 0 03

After the sodium had been distilled onto surface *B* and the pressure of gas evolved measured by means of a calibrated McLeod, the gas was pumped out of the system, and a second distillation of the sodium along surface *B* was carried out Under this treatment a smaller quantity of gas was evolved, ~0 05 μ The leak rate of the system was approximately 0 05 μ per hour

Preparation of blue solution

A quartz ampule previously baked at 830 C for 20 hr was used to prepare the blue solution About 10^{-6} mole of sodium were distilled onto the wall of region *B* while pumping under "stick" vacuum conditions Then 3 ml of degassed liquid ammonia were distilled into region *B* at −78 C forming a blue solution

Evolution of gas from the blue solution

After the blue solution had been prepared, a liquid nitrogen bath was placed around the ampule at region *B* A small pressure of ~1 μ (~5 10^{-8} mole of hydrogen) was measured by means of a calibrated McLeod (There was a trap with a liquid nitrogen bath around it between the McLeod gauge and the ampule)

Study of sodium residue

After the pressure measurements, the ammonia was distilled out of region *B*, leaving behind a sodium residue at the bottom of region *B* The residue was pumped on for about 16 hr under "stick" vacuum conditions Then the residue was heated with a yellow flame distilling the sodium along surface *B* A small quantity of gas was evolved as measured by a calibrated McLeod gauge The pressure was 1 0 μ A sample of this gas was found to contain hydrogen as determined by a mass spectrometric analysis After this gas was pumped off, the sodium was distilled a second time along the wall in region *B* with the evolution of a smaller quantity of gas 0 35 ± 0 03 μ Similar results were obtained using a quartz ampule that had been baked at 600°C for 20 hr under "stick" vacuum conditions

Test of quartz surface

In order to determine whether the gas evolution might be due to a reaction between the sodium metal and adsorbed ammonia either on the quartz surface or the sodium metal itself, the following procedure was used After 10^{-6} mole of sodium were distilled onto a quartz ball in region *A*, 3 ml of liquid ammonia were distilled into region *B* at −78°C During this procedure the sodium film on the surface of the quartz ball located in region *A* was exposed to the ammonia-vapour The liquid ammonia was then distilled out of region *B*, and the coated ball transferred to region *B* The system was again pumped on for about 16 hr under "stick" vacuum conditions Then the sodium was distilled from the glass ball surface onto the wall of region *B* The pressure of the gas given off was 0 35 μ After this gas was pumped off, the sodium was distilled a second time along the wall of region

B with the evolution of a smaller quantity of gas ~0 05 μ These results agree with those shown in Table 1 and suggest that the gas evolution obtained by heating the sodium residue with a yellow flame is due to a partial decomposition of the residue

DISCUSSION OF RESULTS

The possibility that hydrogen gas is either occluded or adsorbed in the sodium residue independent of any chemical reaction that has occurred in the blue solution has been considered previously (1) Evidence was presented indicating that when sodium metal is distilled onto the surface of a glass ball located in region *A* (Fig 1) under conditions in which hydrogen gas is both evolved and pumped on, the hydrogen gas in not introduced into the distilled sodium This evidence was obtained by transferring the coated ball to region *B* and then, under defined experimental conditions, distilling the sodium onto surface *B* The evolution of hydrogen gas was shown to be due probably to a chemical reaction on the surface of the glass rather than to a degassing of the sodium upon its distillation These considerations suggest that the source of hydrogen in the sodium residue from a dilute solution of sodium in liquid ammonia is probably the result of a prior chemical reaction in the blue solution rather than a reaction of the evolved hydrogen gas with the "pure" sodium residue

From a viewpoint of simplicity, sodium amide and sodium hydride are suggested as two possible sources of hydrogen in the residue from a dilute solution of sodium in liquid ammonia In the presence of catalysts, sodium amide is a decomposition product in the preparation of a dilute solution of sodium in liquid ammonia,(2) while sodium hydride has been observed in the reaction of molten sodium with ammonia in the preparation of sodium amide (2)

When care is taken to prepare a dilute solution of sodium in liquid ammonia at low temperatures, there is no evidence for the presence of sodium amide (1,3) This suggests that sodium amide is not the source of hydrogen in the residue but rather that sodium hydride is

An estimate has been made for the per cent "hydride" in the sodium residue This was done by comparing the pressure of hydrogen evolved from heating the residue with the pressure of hydrogen evolved from reacting sodium that had been distilled onto a quartz ball with excess degassed water on the vacuum line From the ratio (0 95/24 0 + 0 95) it is estimated that there is 3 8 per cent hydride present in 10^{-6} mole of the sodium residue

CONCLUSIONS

The residue from a dilute solution of sodium in liquid ammonia is not "pure" sodium but contains a source of hydrogen, which may be tentatively identified as sodium hydride This evidence suggests that not all the hydrogen formed from the reaction of the dilute solution of sodium in liquid ammonia with the strongly adsorbed water at −78°C is evolved as hydrogen gas, but that some remains behind in the blue solution

---

(2) R Levine and W Fernelius, *Chem Rev* **54**, 449 (1954)

(3) M C R Symons, *Quart Rev* **13**, 107 (1959)

J. Inorg. Nucl. Chem. 1963. Vol. 25, pp. 923 to 925. Pergamon Press Ltd. Printed in Northern Ireland

SOME PROPERTIES OF THE PLATINUM IODIDES

G. R. ARGUE and J. J. BANEWICZ
Texas Research and Electronic Corporation, Dallas, Texas

(*Received* 2 *May* 1962, *in revised form* 4 *September* 1962)

Abstract—Iodides of Pt, PtI_2, PtI_3, and PtI_4 have been prepared, their X-Ray diffraction patterns obtained, and the magnetic susceptibilities determined. PtI_2 was found to be diamagnetic with susceptibility independent of temperature. The temperature dependence of the diamagnetic susceptibility of PtI_3 and PtI_4 was ascribed to impurities. The contribution to the susceptibility per Pt-I bond was found to be essentially the same in all three iodides.

IN the course of an investigation of the electrolysis of I_3^- systems with platinum electrodes, extensive corrosion of the platinum was noted. The formation of a deep red colour characteristic of platinum iodide complexes in a capsule in which platinum and potassium tri-iodide solution had been sealed indicated the direct reaction of the platinum and the iodide. Furthermore, in capsules when a bias was applied between two platinum electrodes, platinum black was observed to form at the cathode. To study this phenomenon, the iodides of platinum were prepared. PtI_2, PtI_3, and PtI_4 have been reported in the literature,$^{(1)}$ but no crystallographic information is available on these compounds. The only information available on the magnetic properties of these compounds was apparently obtained at room temperature.$^{(2)}$ The existence of PtI_3 has been questioned in the literature. It was hoped that from the crystallographic and magnetic susceptibility studies, some elucidation could be made of the structure and existence of the three platinum iodides.

EXPERIMENTAL

PtI_3 was prepared by the addition of potassium iodide solution to cold chloroplatinic acid. The black precipitate was washed thoroughly with water and acetone and dried at 100°C. Several samples of the compound were analysed by thermal decomposition to platinum at 500°C. The results of these analyses are in Table 1.

TABLE 1. THERMAL DECOMPOSITION OF PtI_3 AT 500°C

Wt. of Sample (g)	Wt. of Residue (g)	Pt (%)	Pt Theoretical (%)
0.1574	0.0533	33.8	33.9
0.2603	0.0880	33.8	
0.1621	0.0536	33.2	

PtI_2 was prepared by the slow decomposition of PtI_3 at 270°C. After heating for a period of about 15 hr, the amount of iodine lost gave a composition corresponding to PtI_2. This material was sealed in an evacuated Pyrex capsule, and tempered for 48 hr at 100°C. One sample of the tempered platinum iodide was decomposed to platinum by heating at 500°C. The amount of platinum again agreed to within one part per thousand of that expected for PtI_2. PtI_4 was prepared by the direct reaction

---

(1) J. W. MELLOR, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. S6. Longman, Green, London (1937).

(2) YA. K. SYRKIN and V. I. BELOVA, Izvest. Sektora Platiny i Drug. Blagorod. Metal. **25,** 153 (1950).

TABLE 2.—X-RAY DIFFRACTION DATA FOR IODIDES OF PLATINUM

PtI_2		PtI_3		PtI_4	
d	Relative intensity	d	Relative intensity	d	Relative intensity
2.934	(100)	3.005	(100)	3.180	(100)
5.15	(83)	2.901	(76)	3.005	(76)
1.979	(77)	2.486	(70)	3.71	(72)
3.025	(73)	1.963	(54)	1.979	(60)
4.89	(63)			1.963	(52)
3.46	(57)				

of weighted amounts of platinum and iodine in an evacuated Pyrex capsule at 150°C. The platinum iodide obtained was tempered at 90°C for about one hundred hours. All three of the iodides were black in colour.

X-ray diffraction patterns were run on the iodides, using a North American-Philips diffraction unit with a copper tube. The plane spacings obtained, together with their relative intensities, are shown in Table 2. A Faraday method was used to determine the magnetic susceptibilities of samples of all three of the iodides, at temperatures from 90 K to about 400 K at field strengths of 500, 1100 and 1700 oe. The experimental apparatus and procedures have been previously described(3). All three of the iodides had diamagnetic susceptibilities entirely independent of field strength. The data obtained are shown in Table 3.

TABLE 3.—MAGNETIC SUSCEPTIBILITY DATA FOR PLATINUM IODIDES

PtI_2		PtI_3		PtI_4	
Temp (°K)	$\chi_m \times 10^6$	Temp (°K)	$\chi_m \times 10^6$	Temp (°K)	$\chi_m \times 10^6$
83	102	83	90.4	81	185.7
300	101	300	134.8	300	200
433	102	400	142.8	378	202.5

RESULTS AND DISCUSSION

The PtI_2 and PtI_4 crystallographic data could not be fitted to the cubic, hexagonal, or tetragonal systems. The PtI_3, on the other hand, fitted the cubic system with a value of "*a*" equal to 11.3 Å. The crystallographic data indicated that the PtI_3 was not a mixture of PtI_2 and PtI_4, but a separate compound.

The temperature independent diamagnetic susceptibility of platinum diiodide is close to the value which would be expected for diamagnetic contributions from two iodide ions, according to KLEMM(4). If the compound is ionic, it appears that the actual contribution of the iodide ions must be somewhat less than KLEMM's value, and that the Pt^{+2} species contributes only a small amount to the susceptibility. On the other hand, it is more likely that the bonding is covalent, rather than ionic, and that the contribution of Pt-I bond is 51×10^{-6} e.m.u. per formula weight. This value is somewhat lower than the 61×10^{-6} e.m.u. reported by SYRKIN and BELOVA(2). The susceptibilities of the tri- and tetra-iodides are temperature dependent. The numerical data can be fitted to the equation

$$\chi + b = \frac{c}{T + \Delta}$$

---

(3) J. H. BANEWICZ, R. F. HEIDELBERG and A. H. LUXEM, *J. Phys. Chem.* **65**, 615 (1961).

(4) W. KLEMM, *Z. Anorg. Chem.* **284**, 377 (1940), **246**, 347 (1941).

where b is the total diamagnetic contribution of the constituent ions. Δ is the Weiss constant, and C is the apparent Curie constant. The values for the three constants are shown in Table 4. The value of b for both iodides should correspond to the total diamagnetic contribution of the constituent atoms. The major contribution to b is made by the iodide in both the triiodide and tetraiodide.

TABLE 4.—WEISS-CURIE CONSTANTS

	b	c	Δ
PtI_3	161×10^{-6}	717×10^{-3}	26.2
PtI_4	219×10^{-6}	9.85×10^{-3}	202.0

The bonding in PtI_3 and PtI_4 is almost certainly covalent. In this case, the contribution to susceptibility per Pt-I bond is 54×10^{-6} e.m.u. for PtI_3, and 55×10^{-6} e.m.u. for PtI_4. The close agreement with the value for PtI_2 would then indicate that the bonding is the same in all cases. SYRKIN and BELOVA reported the contribution per Pt-I bond in PtI_4 to be 45×10^{-6} e.m.u. per formula weight, a value different from the contribution of the Pt-I bond in PtI_2. The temperature dependence is probably due to traces of some paramagnetic impurity. In PtI_4 there is probably a small excess of platinum metal. From the magnitude of the Curie constant, the approximate amount of free platinum in the iodide is computed to be of the order of one part per thousand. The nature of the impurity in the PtI_3 is not known.

J Inorg Nucl Chem, 1963, Vol 25, pp 927 to 932 Pergamon Press Ltd Printed in Northern Ireland

ASSOCIATION IN CYCLIC BORONATES AND BORATES

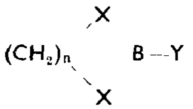
A FINCH and P J GARDNER
Chemistry Department, Royal Holloway College, University of London,
Egham, Surrey, U K

(*Received* 20 *November* 1962, *in revised form* 10 *January* 1963)

Abstract –The molecular weights of some cyclic boron compounds have been studied over a wide concentration range Olan derivatives were far more associated than their inan analogues The degree of association of some inans was concentration-independent Modes of association are proposed

SEVERAL references to molecular weight determinations of cyclic boron compounds at isolated concentrations are to be found in the literature (1,2) There are also many reports of anomalous physical properties (e g, boiling point, viscosity) of cyclic derivaties relative to their acyclic analogues (1,3,4,5)

Investigation of a series of compounds of the type



n = 2, 3
Y = Cl, ϕ, OR
X = O, S
R alkyl

indicates two distinct modes of association (a) concentration-dependent association and (b) concentration-independent association, with the occasional possibility of both The results confirm the predictions of DALE(6) on the relative stabilities of trigonal and tetrahedral boron in five- and six-membered rings It is clear, from this work, that any molecular weight datum obtained at an isolated concentration should be accepted with reservation

EXPERIMENTAL

General procedure Compounds (X = S, Y = ϕ) were prepared by condensing phenyl boron dichloride with the appropriate dithiol All others were prepared by condensing boron trichloride with the appropriate diol followed by alcholysis for the ester derivatives The majority of the derivatives, being moisture-sensitive were handled in a dry-box, they were distilled under reduced pressure immediately prior to use Precautionary measures were taken to ensure the absence of pyrolysis or hydrolysis throughout cryoscopic measurements The benzene solvent, of specially purified cryoscopic grade (B D H) was stored over sodium

Apparatus The cryoscopic cell was of all glass construction and similar to that of ZEMANY(7) Agitation was effected by means of a chromium-plated stirrer actuated by an external solenoid The intermittent pulse to the solenoid was supplied by a slowly-rotating cam operating a micro-switch The temperature-sensitive element was a thermistor (F2311/300 Standard Telephone and Cables Ltd) incorporated in a Wheatstone bridge

Calibration and errors Using the described equipment, differential temperature measurement was

---

(1) R J BROTHERTON and A L MCCLOSKEY, *J Org Chem* **26,** 1668 (1960)

(2) E W ABEL, S H DANDEGAONKER, W GERRARD and M F LAPPERT, *J Chem Soc* 4697 (1956)

(3) J A BLAU, W GERRARD and M F LAPPERT, *J Chem Soc* 4116 (1957)

(4) J A BLAU, W GERRARD, M F LAPPERT and B A MOUNTFIELD and H PYSZORA *J Chem Soc* 380 (1960)

(5) S H ROSE, *Diss Abs* **22,** 2185 (1962)

(6) J DALE, B HARGITAY and A J HUBERT, *J Chem Soc* 910, 922 and 931 (1961)

(7) P D ZEMANY, *Analyt Chem* **24,** 348 (1952)

accurate to ±0 002 C Assuming the resistance/temperature relation[8,9] for a thermistor to be $R = A \exp [B/T]$, the constants (A, B) were obtained by comparison with a platinum resistance thermometer (Degussa Hanau) over the range 0–6°C coupled to a six-inch potentiometric recorder sensitive to 0 02 C The thermistor was also directly calibrated by determining the constant C in the standard form of the depression equation $M_2 = Cm_2/\Delta R$, where M_2 = molecular weight of solute, m_2 = mass of solute, and ΔR = freezing-point depression in ohms The value of this constant was found to be within ±1 per cent of that calculated from the approximate expression $C = M_1 R R_0 B/Hm_1$, where R = gas constant R_0 = resistance at T_0, ΔH latent heat of fusion of the solvent and T_0 = freezing point of pure solvent Since the benzene/naphthalene system is ideal to almost eutectic concentrations[10] it is legitimate to use the experimental value of C in computing molecular weights, cryoscopically determined in benzene

Values of the cryoscopic constant K_f, derived from the equation $K_f = m_1CT_0^2/R_0B$ were 5123 ± 100 for benzene (Lit [11] 5120), and 7161 ± 100 for nitrobenzene (lit [11] 7200) Test runs over the concentration range 0 01–0 6 M on phenyl boron dichloride and tri-n-butyl borate were made, giving molecular weights of 161 (calculated 158 8) and 226 (calculated 232 2) respectively The reproducibility of individual runs was *ca* 0 3 per cent

The reproducibility of runs on the compounds studied varied between ±0 3 and ±2 per cent, dependent on their stability The approximations involved in using the standard colligative depression equation were estimated for a hypothetical compound of molecular weight 150 ideally dissolved in benzene and amounted to 0 4, 1 5 and 3 7 per cent at the concentrations 0 05, 0 2 and 0 5 M respectively The accuracy of the experimental data hence depends largely on the purity and stability of the compounds rather than the precision or accuracy of the experimental method

RESULTS AND DISCUSSION

Molecular weights at 0 5M, 0 2M and 0 5M concentrations are listed in the Table and the variation of cryoscopic depression with concentration for several compounds is shown in Fig 1

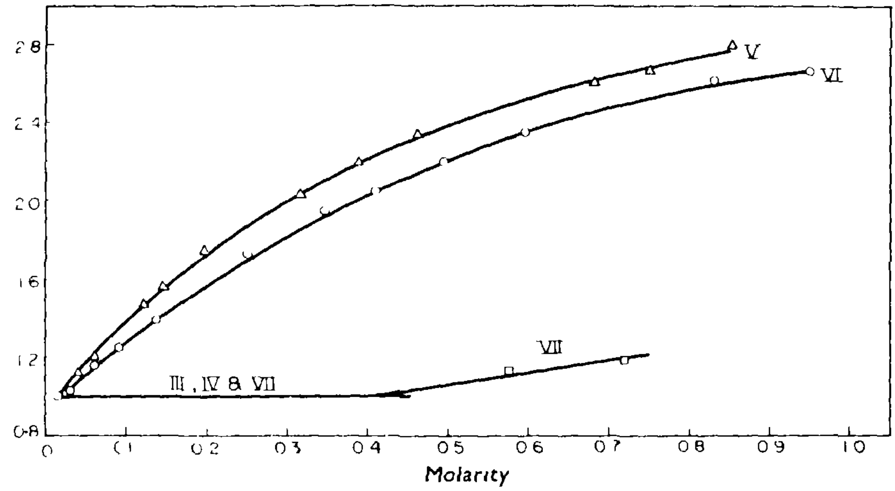


FIG 1 —Graphs of degree of association (α) vs Molarity III Phenyl boron dichloride IV Tri-n-butyl borate V 2-(2′-chloroethoxy) 1 3,2-dioxaborolan VI 2-(n-butoxy) 1,3,2-dioxaborolan VII 2-(2′-chloroethoxy) 1,3,2-dioxaborinan (experimental points for III, IV and VII are omitted between 0 0 and 0 45 molar)

---

[8] J A BECKER, C B GREEN and G L PEARSON, *Bell Syst Tech J* **26**, 170 (1947)

[9] H A SKINNER (Editor), *Experimental Thermochemistry*, Vol 2, p 168, Interscience, New York (1962)

[10] R K MCKULLAN and J D CORBETT, *J Chem Educ* **33**, 313 (1956)

[11] WEISSBERGER (Editor) *Techniques of Organic Chemistry Vol* 7 Organic Solvents Interscience, New York (1955)

MOLECULAR WEIGHTS AT THREE MOLARITIES

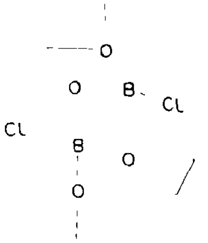
	Compound	b p (C mm)	Molecular weight (Degree of Association) 0 05M	0 2M	0 5M	Calcd Mol wt
I	OCH_2CH_2OBCl	35-40 0 05	130(1 22)	200(1 88)	260(2 44)	106 3
			130(1 22)*	168(1 58)*	220(2 07)*	
II	$OCH_2CH_2CH_2OBCl$	22-24 0 05	135(1 12)	133(1 12)	135(1 12)	120 3
			130(1 08)*	130(1 08)*	130(1 08)*	
III	ϕBCl_2	66 18	161(1 01)	161(1 01)	—	158 8
IV	$(Bu^nO)_3B$	232 760	226(0 98)	226(0 98)	—	230 2
V	$OCH_2CH_2OBOCH_2CH_2Cl$	59-60 0 05	152(1 01)	305(2 03)	274(2 49)	150 4
VI	$OCH_2CH_2OBOBu^n$	58-60 0 05	146(1 01)	233(1 62)	346(2 40)	144 0
VII	$OCH_2CH_2CH_2OBOCH_2CH_2Cl$	57-58 0 05	169(1 03)	169(1 03)	189(1 15)	164 4
VIII(12)	SCH_2CH_2SBCl	24-25 0 05	141(1 02)	141(1 02)	—	138 5
IX(12)	$SCH_2CH_2CH_2SBCl$	52 0 1	165(1 08)	165(1 08)	—	152 5
X(12)	$SCH_2CH_2SB\phi$	90-92 0 05	179(0 99)	179(0 99)	—	180 1
XI(12)	$SCH_2CH_2CH_2SB\phi$	110-111 0 05	196(1 01)	196(1 01)	—	194 1

* in nitrobenzene solvent all others in benzene

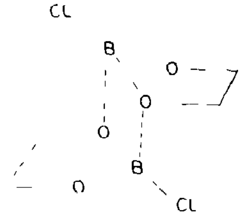
(12) A FINCH and E J PEARN, Unpublished work

The acyclic compounds phenyl boron dichloride and tributyl borate (III, IV) and the sulphur compounds (VIII X XI) are monomeric at all concentrations studied. All others show association, the effect being especially marked and concentration-dependent in the five-membered (olan) structures. Considering these first, four models for association may be examined

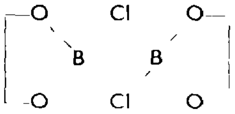
(1) Boron-oxygen bridging (x = Cl)



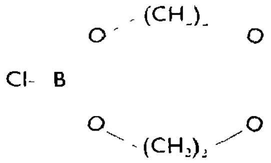
(2) Four-centre interaction (x = Cl)



(3) Chlorine bridging (X = Cl)



(4) Ten-membered ring formation (X = Cl)



or combinations of these

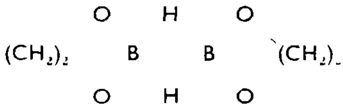
Large-ring formation (4) may be dismissed, since, as seen in the Figure, the degree of association is strongly concentration-dependent, and the energy required for breaking a B—O bond (*ca* 110 kcal/mole[13]) is not available on dilution. In this model alone the boron retains the sp^2 (trigonal) configuration, hence nuclear magnetic resonance measurements might be of value. Molecular models show that the ten-membered system is strain-free, hence its independent existence is not precluded.

Since the olan esters (V) and (VI), like the parent compound (I), show similar strongly concentration-dependent association, it is reasonable to ascribe this primarily to (1). From the physical properties, e.g. viscosity, vapour-pressure, boiling point, of the pure phases, as well as by extrapolation of the molecular weight *vs* concentration data, it is obvious that these compounds are associated considerably beyond the dimer ($\alpha = 2$) stage. However, the inapplicability of colligative-property equations to these conditions prevents the precise estimation by the usual techniques. This suggests that some form of stacking, as in (I), is operative. As expected from its higher dielectric constant, the use of nitrobenzene as solvent reduced the degree of association.

---

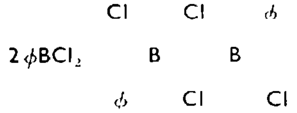
[13] T. CHARNLEY, H. A. SKINNER and N. B. SMITH *J. Chem. Soc.* 2288 (1952)

Compound (II) is of special interest since the six-membered (inan) skeleton, unlike the olan analogue, is relatively strain-free, and hence less tendency for change to the tetrahedral sp^3 configuration ($sp^2 \rightarrow sp^3$) would be predicted. The comparatively small association observed (α = 1.1 in both benzene and nitrobenzene) is well outside experimental error and independent of concentration; this is in direct contrast with the behaviour of the olan system. It is possible, therefore, that a different mechanism, e.g. chlorine bridging (2) is now operative. Similarly, the dithioborinan is also slightly associated in a concentration-independent manner. If it is assumed that a degree of association of 1.1 represents a monomer-dimer equilibrium, $2A \rightleftharpoons A_2$, it is difficult to understand why this should not be dependent on concentration. This form of bridging is formally similar to the hydrogen bridging proposed in a recent dissertation[5] for 1,3,2-dioxaborolan



$$\begin{array}{ccccc} & O & H & O & \\ (CH_2)_2 & & B \quad\quad B & & (CH_2)_2 \\ & O & H & O & \end{array}$$

No evidence for stable chlorine bridging in boron compounds could be found in the literature, though the phenomenon is well established for other elements. In this connexion the molecular weight of phenyl boron dichloride was measured under comparable conditions, and a strictly monomeric solution was found at all concentrations. This confirms a previously reported value[2] at a single concentration. This does not preclude chlorine bridging in the inan derivatives. The difference in energy between trigonal and tetrahedral boron configurations is very much greater in the cyclic than the acyclic system. Further, the extent of dimerisation

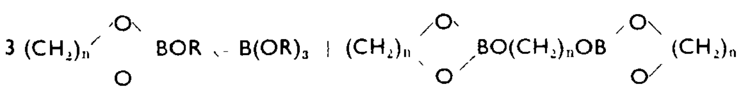


$$2\phi BCl_2 \rightleftharpoons \begin{array}{ccc} Cl & Cl & \phi \\ B & & B \\ \phi & Cl & Cl \end{array}$$

might be expected to be small under ambient conditions.

Association of the inan ester (VII) cannot occur via chlorine bridging; it is slightly concentration-dependent and presumably due to boron-oxygen interaction.

The n-butyl and 2-chlorethyl esters were selected as being of known stability.[14] The apparent high molecular weight of some esters may be due to disproportionation.[6]



The possibility that solvent-solute interaction, i.e. weak π-bonding, occurred was also considered. The ultraviolet spectrum of solutions of benzene, of (II) and of an equimolar mixture of both, all in cyclohexane, were measured in the range 220-290 mμ. No changes in the characteristic B-band at 255 mμ, loss of fine structure or change in band envelope were observed.

---

[14] A. Finch, P. J. Gardner, J. C. Lockhart and E. J. Pearn, *J. Chem. Soc.* 1428 (1962).

In principle this association should be reflected by the appearance in the infra-red spectra of bands associated with $\nu_{B-X\,(bridge)}$ and with corresponding changes in the frequency of ν_{B-X} in the monomeric molecule However, the assignment of ν_{B-Cl} in (I) is equivocal(15) and the region in which boron-oxygen stretching modes are expected to absorb (ca 1300-1440 cm^{-1}) is complex Hence as yet this method has not been successful in distinguishing between the two forms of association

Acknowledgments—It is a pleasure to thank Dr J C LOCKHART for helpful discussion, Messrs B SMETHURST and R LANE for technical assistance and the Petroleum Research Foundation (American Chemical Society) for the award of a pre-doctoral Fellowship (P J G) The recording platinum resistance thermometer was purchased with a grant from the Central Research Fund (University of London), to whom sincere thanks are due

(15) A FINCH, P J HENDRA and E J PEARN, *Spectrochim Acta*, **18**, 51 (1962)

J. Inorg. Nucl. Chem. 1963, Vol. 25, pp. 933 to 944. Pergamon Press Ltd. Printed in Northern Ireland

STUDY OF THE QUINQUEVALENT CHROMIUM COMPOUNDS BY ESR AND OPTICAL SPECTRA

H. KON
NAIG Nuclear Research Laboratory, Kawasaki, Japan

(*Received* 6 *November* 1962, *in revised form* 6 *February* 1963)

Abstract—Quinquevalent chromium complexes of the type $CrOCl_3$ + 1(or 2) RCl, where R = pyridinium, quinolinium, tetramethylammonium (or potassium) ion, were prepared and their electron spin resonance absorptions were observed in solution at room temperature and at 77 K, as well as in polycrystalline form. The results, together with those of the optical absorption spectra, indicate that these complexes have a common paramagnetic structural unit $CrOCl_4$. The observed values of $g_{\parallel}$ and $g_{\perp}$ of this species were explained on the basis of the molecular orbital theory.

The transient, narrow ESR lines with similar feature were also observed during the reduction of $K_2Cr_2O_7$ *(or* CrO_3*) with a variety of acids. They were interpreted as due to some* $Cr^{(V)}$ *oxyion complexes.*

IN the previous communication(1) the author postulated the existence of the quinquevalent chromium compounds in CrO_3-(or $K_2Cr_2O_7$-)conc. H_2SO_4 system to explain the narrow ESR (electron spin resonance) absorption lines which can easily be observed at room temperature and which consist of four narrow lines with uneven intensities, their line widths being from about 1 to 5 G. To the best of the author's knowledge, there are not many ESR observations reported of quinquevalent chromium compounds. CARRINGTON *et al.* first observed ESR signal of $Cr(V)O_4^{3-}$. In remarkable contrast to the case of CrO_3–conc. H_2SO_4 system, however, the ESR line width of CrO_4^{3-} is temperature dependent, broader at higher temperature, and could not be observed above $T = 20°K$.(2) This is the behaviour to be expected not only for CrO_4^{3-} but also for other transition metal ions in general with single unpaired *d*-electron, provided they are placed in the crystalline field with the cubic symmetry or with the nearly cubic symmetry, which, furthermore, is not so strong as to lift the degeneracy of the d-orbitals sufficiently.(3) More recently, SWALEN and IBERS reported the ESR study of peroxychromate ion, $Cr(V)O_8^{3-}$, in polycrystalline form at 20°C. This ion has D_{2d} symmetry, and the ESR line width $\Delta H_{1/2}$ was determined by the numerical analysis to be 23.5 G.(4)

It would be of interest to see whether there are any other compounds of the Cr ion with single unpaired *d*-electron, which show the narrow ESR lines such as those observed in CrO_3–conc. H_2SO_4 system (ca. 1–5 G).

For this purpose, the following complexes of Cr(V) were prepared, and their ESR and optical absorption spectra were observed:

$$K_2Cr(V)OCl_5 \quad \text{and} \quad Cr(V)OCl_3 \cdot RCl,$$

---

(1) H. KON, *Bull. Chem. Soc. Japan*, **35**, 2054 (1962).

(2) A. CARRINGTON, D. J. E. INGRAM, D. SCHONLAND and M. C. R. SYMONS, *J. Chem. Soc.* 4710 (1956).

(3) B. BLEANEY and K. W. H. STEVENS, *Rep. Prog. Phys.* **16**, 141 (1953).

(4) (a) J. D. SWALEN and J. A. IBERS, *J. Chem. Phys.* **37**, 17 (1962),
(b) J. A. IBERS and J. D. SWALEN, *Phys. Rev.* **127**, 1914 (1962).

where R is pyridinium, quinolinium or tetramethylammonium ion These compounds were first synthesized by WEINLAND *et al*,[5,6] who ascertained that Cr is in the quinquevalent state There has been little information available concerning the structure of these molecules, but these complexes may be considered as the analogues of the many, fairly well studied vanadyl complexes, where the crystalline field symmetry surrounding the V ion is shown to have an axial component which is strong enough to make the lowest excited orbital sufficiently high above the ground orbital, thus making the ESR lines easily observable at room temperature [7]

One of the purposes of this paper is to present the detailed results of the ESR, visible and infra-red absorption measurements of the complexes in solution as well as in polycrystalline form Deductions will be made in relation to the nature of the bonds from the standpoint of the ligand field and molecular orbital theory

It was suggested by JABLCZYNSKI and several other workers that during the course of the reduction of CrO_3 or $K_2Cr_2O_7$ by the acids such as formic, oxalic and so on, Cr passes through an intermediate valence state between Cr(VI) and Cr(III), and the results of a series of kinetic studies of these reactions are best understood by assuming the quinquevalent state for Cr [8,9]

In the present report, the above assumption will also be proved by the direct observation of ESR signals, which show the feature similar to the $K_2Cr(V)OCl_5$ and $Cr(V)OCl_3RCl$

EXPERIMENTAL

Chemical procedures

$CrOCl_3RCl$ type compounds were prepared following the method by WEINLAND *et al* [5,6]

About 100 ml of a dilute acetic acid solution (ca 10^{-2} M) of CrO_3 was reduced by passing dry HCl gas through the solution The calculated amount of the base, such as pyridine, quinoline or tetramethylammonium chloride was dissolved in the least possible amount of acetic acid saturated with dry HCl gas By adding the latter solution to the reduced CrO_3 solution, the fine lustrous crystalline precipitate was obtained The colour varied from reddish to dark brown according to the base used It was found that in order to obtain the homogeneous crystalline material, the reduction by HCl gas must be complete before adding the solution of the base, otherwise the precipitate was the mixture of more than one complex of various colours The reduction was best monitored by observing the ESR signals at different stages of the reaction The pattern near the end of the reaction is free from the complication due to by-products Samples were dried and kept over KOH or conc. H_2SO_4 in vacuum The complexes are all very sensitive to the humidity and, therefore, every precaution was taken to prevent the decomposition during the handling The yield was very good for $CrOCl_3RCl$, whereas only a very small amount of cyrstalline material was obtained for K_2CrOCl_5

To observe the transient ESR signals of Cr(V) caused by the reduction with organic acids other than acetic acid, a portion of the dilute stock solution of $K_2Cr_2O_7$ in glacial acetic acid was mixed with the acid with constant stirring until the colour of the solution became dark brown CrO_3 gave rise to the ESR signal simply by dissolving it in the acetic acid

ESR measurement

All the measurements were carried out with Varian Associates model V-4500 spectrometer with 100 kc/s field modulation The field strength was calibrated by measuring the proton resonance frequency with the Hewlett-Packard model 524C electronic counter combined with the 525A frequency converter To determine g-values, the measurement of the resonance field for DPPH (g = 2 0036)

---

[5] R F WEINLAND and W FRIDRICH, *Ber Dtsch Chem Ges* **38**, 3784 (1905)

[6] R F WEINLAND and M FRIEDERER, *Ber Dtsch Chem Ges* **39**, 4042 (1906), **40**, 2090 (1907)

[7] B R MCGARVEY, *J Phys Chem* **61**, 1232 (1957)

[8] K JABLCZYNSKI, *Z Anorg Chem* **60**, 38 (1908)

[9] C WAGNER, *Z Anorg Chem* **168**, 279 (1928)

preceded each spectrum, the kylstron frequency being kept constant throughout a series of measurements

The observations of the polycrystalline ESR were carried out either at room temperature for the solid material or at the liquid nitrogen temperature for the solution The concentration of most of the solution was ca $10^{-2} \sim 10^{-3}$ M When acetic acid was used as solvent for $CrOCl_3 RCl$ the signal looked like some superposition of more than one spectrum and there was usually remarkable decrease in signal intensity Normal line shape and intensity were recovered by passing the dry HCl into the solution

Optical spectra

The visible absorption in solution and the infra-red absorption in KBr press were measured by Hitachi Co model EPS II spectrophotometer and Japan Spectroscopic Manufacturing Co model DS-401G grating infra-red spectrophotometer, respectively Dried acetic acid saturated with HCl gas, or nitrobenzene was used as solvent

RESULTS

$CrOCl_3RCl$, K_2CrOCl_5

The ESR spectra of these complexes (R = pyridinium, quinolinium or tetramethylammonium ion) in solution at room temperature are virtually all identical in their g-values, line widths and the average hyperfine splittings due to ^{53}Cr (the natural abundance = 9 55 per cent, the nuclear spin number $I = \frac{3}{2}$), as summarized in Table 1 In Fig 1 is shown a reproduction of a typical solution spectrum for pyridinium complex The following features are worthy to note

TABLE 1 *g*-VALUES, LINE WIDTHS AND AVERAGE HYPERFINE-SPLITTINGS OF $CrOCl_3RCl$ AND K_2CrOCl_5 IN SOLUTION AT ROOM TEMPERATURE

Sample	*g* (Solution)†	Line width (G)** $\Delta H_{\max\ \text{slope}}$	Av hfs (G)**
K_2CrOCl_5/ $CrORCl_4$	1 9877	2 8*	19 7
R = pyridinium	1 9877	2 8* 2 1‡	19 9
R = quinolinium	1 9880	2 6* 2 0‡	19 9
R = tetramethyl-ammonium	1 9875	2 7* 1 9‡	19 8

* In glacial acetic acid, ‡ In nitrobenzene

† Accurate to ca ±0 0003, ** Accurate to ca ±0 1 G

First, the observed ESR lines are all very narrow, even narrower than in the vanadyl ion solutions of about the same concentration as in the present study (10) In general, the ESR line width is known to be affected by many complicated factors, but it may be deduced from the above results that the electrostatic field surrounding the Cr(V) ion is strongly perturbed from the cubic symmetry since, otherwise, a low lying excited level may cause a short spin-lattice relaxation time and may result in a very broad line as, for example, in the Ti^{3+} alum (3)

The resolution of the two inner components of the ^{53}Cr hyperfine structure is partly disturbed by the superposition on the main line due to the abundant ^{52}Cr

(10) R N ROGERS and G F PAKE, *J Chem Phys* 33, 1107 (1960)

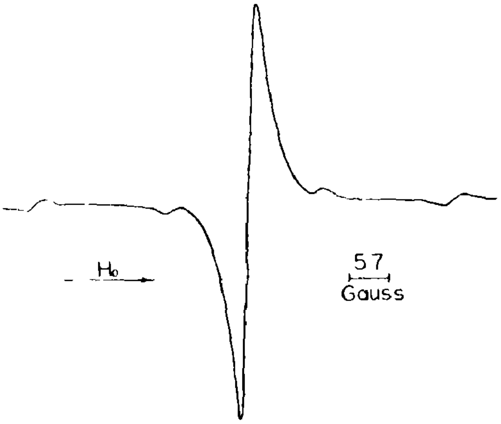


FIG. 1 A representative ESR absorption curve of CrOCl$_4$RCl in solution at room temperature (R = pyridinium ion) The solvent is the acetic acid saturated with HCl gas

complex (The situation is better in the nitro-benzene solution where the lines are narrower) Nevertheless, it can be seen that there is little variation of the line width of the individual hyperfine component with the nuclear quantum number I_z Such variation of the line width has been observed in several complexes so far studied (as well as in the cases to be discussed in the next section), and the origin was first explained by McCONNELL$^{(11)}$

Recently, ROGERS and PAKE$^{(10)}$ formulated the line width as a polynomial in I_z, based on the general theory of KIVELSON$^{(12)}$

$$
\begin{aligned}
1/T_2 &= \pi\sqrt{(3)}\,(a_1 + a_2 I_z + a_3 I_z^2), \text{ where}\\
a_1 &= \tau_c\,\{(7/45)(\Delta\gamma H_0)^2 + 63\,b^2/16\} + K,\\
a_2 &= -\tau_c\{(7/15)\,b\,\Delta\gamma H_0\},\\
a_3 &= \tau_c\,\{b^2/10\}, \text{ and}\\
\Delta\gamma &= (\beta/\hbar)(g_{\parallel} - g_{\perp}),\ b = (2/3)(A_{\parallel} - A_{\perp})
\end{aligned}
$$

H_0 is the external magnetic field strength, τ_c the correlation time and K is a constant to take into account all relaxation mechanisms not sensitive to the nuclear orientation The above formula was shown to explain the line width variation in VO^{2+} aq solution successfully

Thus under ordinary conditions the variation of the hyperfine line width with I_z is governed by the two parameters $\Delta\gamma$ and b, the anisotropies of g- and the hyperfine interaction tensors, respectively Since the anisotropy in g-tensor of the complexes under discussion estimated from the spectrum of the frozen solution of CrOCl$_4^-$ ($g_{\parallel} = 2\ 00_8$, $g_{\perp} = 1\ 97_4$, vide infra), $\Delta g = 0\ 03_4$, is not particularly smaller than other cases where the variation of the hyperfine line width is remarkable (for ex, in vanadyl porphyrins,$^{(13)}$ $\Delta g = g_{\parallel} - g_{\perp} = 0\ 042$), the apparent absence of the variation in hyperfine line width in the present case may be explained by an approximately isotropic hyperfine interaction tensor

---

(11) H M McCONNELL, *J Chem Phys* **25**, 709 (1956)
(12) O KIVELSON *J Chem Phys* **33**, 1094 (1960)
(13) E M ROBERTS, W S KOSKI and W S CAUGHEY, *J Chem Phys* **34**, 591 (1961)

The average hyperfine splitting is larger than in Cr^{+} cyanide complex(14) (13 8 G) in which the unpaired spin is considered to be in $3d_{xy}$ orbital as in the present complexes

The fact that all these compounds show the ESR patterns which are identical within the experimental accuracy, indicates the existence in solution of the same paramagnetic species common to the systems The frozen solutions (*)(77°K) also exhibit identical ESR patterns such as the one shown in Fig 2, from which one may conclude that the paramagnetic species has an axial (or nearly axial) symmetry in solution Thus one reasonable structure of the common paramagnetic species may be assumed as,

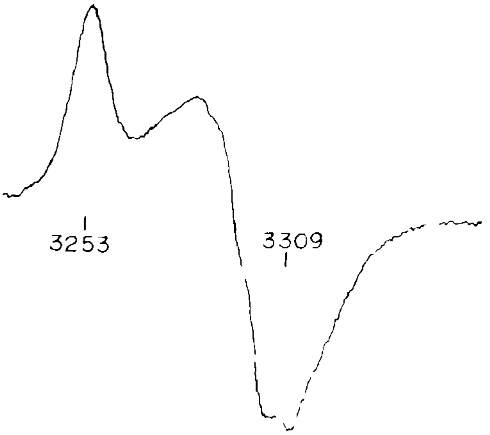
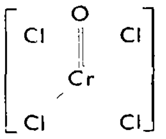


FIG 2 - A representative ESR absorption curve of $CrOCl_4RCl$ in frozen solution at 77°K (R = pyridinium ion) The solvent is the acetic acid saturated with HCl gas Field strengths are shown in gauss



The estimated values of $g_{\parallel}$ and $g_{\perp}$ are(15)

$$g_{\parallel} = 2\ 00_8 \quad \text{and} \quad g_{\perp} \quad 1\ 97_4$$

from which $g_0 = (\frac{1}{3})(g_{\parallel} + 2g_{\perp}) - 1\ 98_5$ in approximate agreement with the g-values observed in solution (1 9875–1 9880, Table 1)

The estimated values are subject to a small correction for the unresolved ^{53}Cr hyperfine structure which is only barely discernible under the conditions of the present study, also the estimation is based upon the assumption of the δ-function for the crystalline line shape, and the Gaussian broadening must be taken into accou implying little exchange interactions between the molecules, since the solution i sufficiently dilute (10^{-2}–10^{-3} M) The same applies to the estimation of g-val from the frozen solution spectra in the next section

---

* Acetic acid saturated with HCl was used as solvent When nitrobenzene was used as solvent, the observation was disturbed by the remarkable saturation broadening

(14) I BERNAL and S E HARRISON, *J Chem Phys* **34**, 102 (1961)

(15) R H SANDS, *Phys Rev* **99**, 1222 (1955)
For the more recent and rigorous analysis of the powder ESR spectra, see for ex , Reference (4b), and H R GERSMANN and J D SWALEN, *J Chem Phys* **36**, 3221 (1962)

On the other hand, the ESR patterns of the crystalline powder diluted with dry *KCl powder are different depending* on the organic base used, as shown in Fig 3

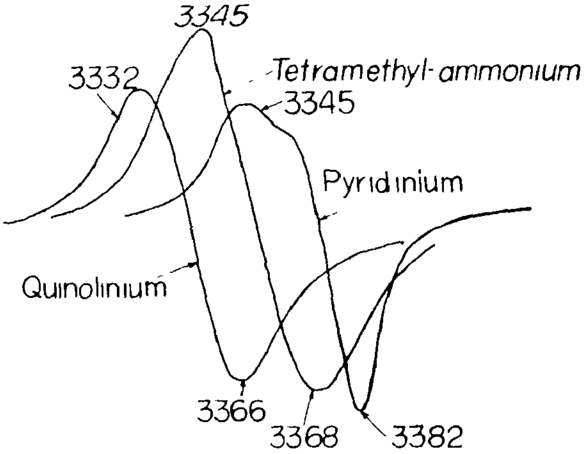


FIG 3 —Polycrystalline ESR patterns of pyridinium, quinolinium and tetramethyl-ammonium complex at room temperature Field strengths are shown in gauss The relative positions of the three curves are arbitrary

This can be explained as the result of the considerably strong interactions between the molecules, and the apparent g-values estimated and listed in Table 2 should be taken as only approximate

TABLE 2 —APPARENT g-VALUES OF POLYCRYSTALLINE POWDER*

Sample	$g_{\parallel}$	$g_{\perp}$	g_0	$(g_{\parallel} + 2g_{\perp})/3$
Pyridinium complex	2 000	1 978		1 985
Quinolinium complex	1 991	1 991		1 991
Tetramethyl-ammonium complex	1 989	1 989		1 989

* Uncertainty in measurement ca ±0 001

In harmony with the above observations, the visible absorption spectra of nitrobenzene solution at room temperature are also almost identical in the four systems There are at least three absorption bands with the peaks at 18,000, 22,400 (sh) and 23,500 cm^{-1} as shown in Fig 4

The results of the infra-red absorption measurements were summarized schematically in Fig 5 Each absorption pattern of pyridinium-, quinolinium- and tetramethyl ammonium chloride is contrasted with that of the respective Cr complex One can easily see there, that the absorption of the complex (except for K_2CrOCl_5) is composed of the slightly shifted lines from the base itself plus a few new absorptions which appear in the range 870–1020 cm^{-1} This would mean that in the crystals the bases exist in the form of pyridinium, quinolinium and tetramethylammonium

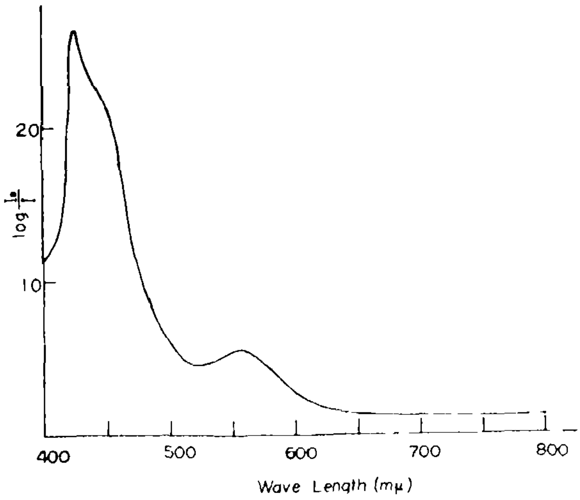


FIG 4 —A visible absorption spectrum of $CrOCl_3RCl$ in nitrobenzene solution (R = quinolinium ion)

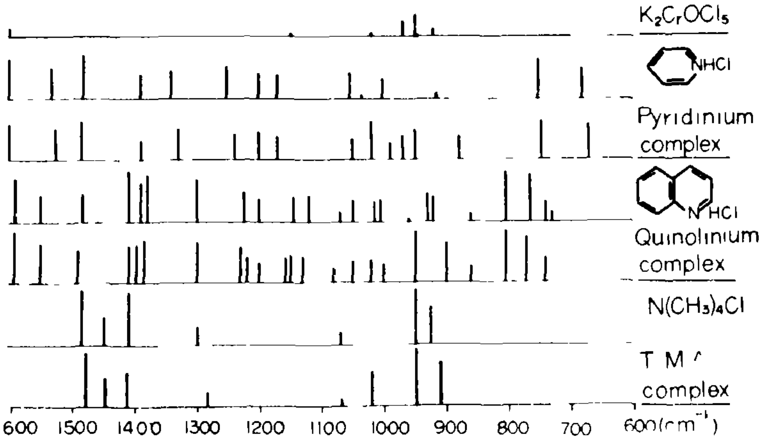


FIG 5 —Infra-red absorption spectra of K_2CrOCl_5, and $CrOCl_3$ RCl (R = pyridinium, quinolinium and tetramethylammonium ion) The lengths of the lines are approximately proportional to the observed absorption intensity

ion, respectively, without being perturbed seriously The 950 cm^{-1} band observed in K_2CrOCl_5 may be assigned to the Cr–O stretching vibration This is comparable to the V–O stretching frequencies in $VOCl_3$ (1035 cm^{-1}) and in VO-etioporphyrin-I (995 cm^{-1})(16)

Miscellaneous quinquevalent Cr *systems*

As was mentioned in the previous section, a variety of narrow ESR signals are obtained as the result of the reaction of $K_2Cr_2O_7$ with various acids such as trifluoro acetic, oxalic-, lactic- or citric acid and of the reaction of CrO_3 with acetic acid The signal shows that the paramagnetic species are unstable and the life time varies

(16) J G ERDMAN, V G RAMSAY, N W KALENDA and W M E HANSON, *J Amer Chem Soc* **78**, 5844 (1956)

considerably with the system from several minutes to a week Unfortunately, the attempts to isolate the paramagnetic compounds have been unsuccessful so far and the composition remains unknown However, it seems valid to say that the paramagnetic species are some unstable reduction products of $K_2Cr_2O_7$ (or CrO_3) by the acids and are stabilized by the complex formation with the acids or some oxidation products of the acids

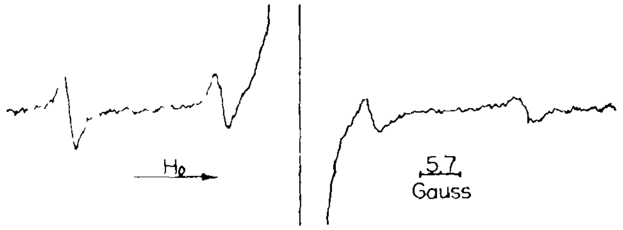


FIG 6 ESR absorption curve of $K_2Cr_2O_7$ CF_3COOH system at room temperature

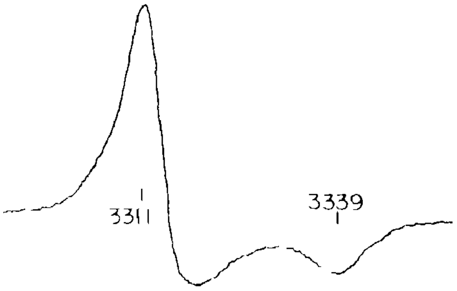


FIG 7—ESR absorption curve of $K_2Cr_2O_7$—CF_3COOH system frozen at 77 K The field strengths are indicated in gauss

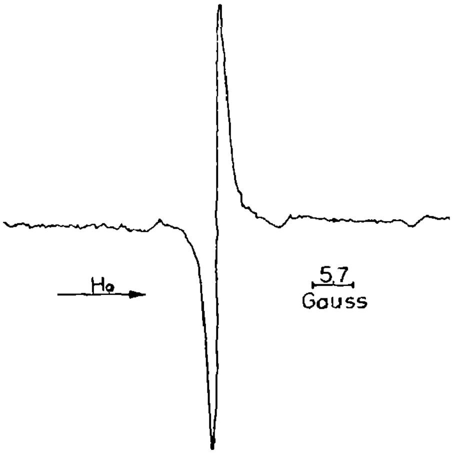


FIG 8—ESR absorption curve of $K_2Cr_2O_7$ - oxalic acid system at room temperature (Solvent acetic acid)

The results of ESR observation, especially the fact that all observed lines are very narrow, are best interpreted by assuming the complexes of some quinquevalent Cr oxyions, such as CrO^{3+} or CrO_2^+ Considering that the possible complexing agents are likely to be mononegative, bi- (or mono-) dentate ions, CrO_2^+ seems more plausible

(1) $K_2Cr_2O_7$ *in* CF_3COOH, *Oxalic acid plus* $K_2Cr_2O_7$ *in glacial acetic acid*, CrO_3 *in glacial acetic acid* The ESR patterns of the solutions at room temperature and at 77°K are shown in Figs 6–11 The general aspects common to these systems can be summarized as follows.

The line width of the hyperfine component increases monotonically from low to high field This indicates, according to the theory by MCCONNELL(11) and ROGERS *et al*,(10) that the hyperfine interaction tensor is fairly anisotropic The pattern of the

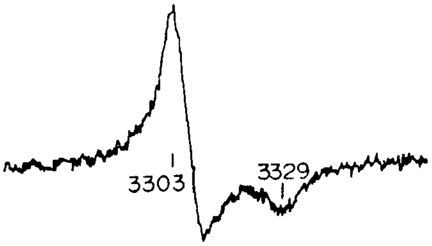
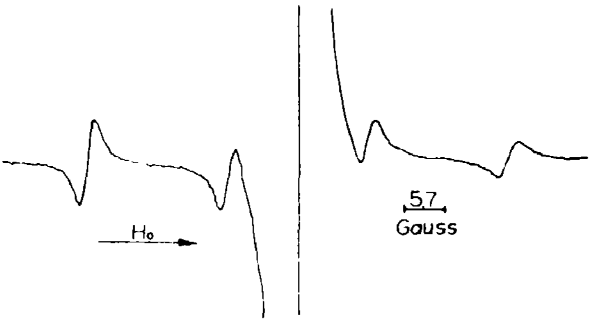


Fig. 9 —ESR absorption curve of $K_2Cr_2O_7$–oxalic acid system frozen at 77 K (Solvent – acetic acid) The field strengths are in gauss

Fig 10 —ESR absorption curve of CrO_3–acetic acid system at room tempearture



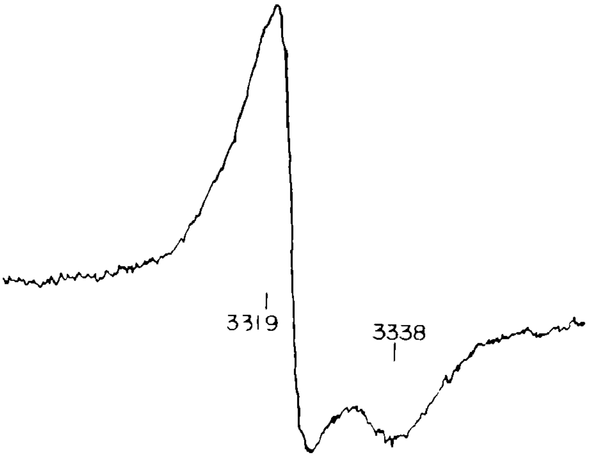


Fig. 11 – ESR absorption curve of CrO_3 acetic acid system frozen at 77 K Field strengths are in gauss

frozen solution shows the characteristic feature of the crystalline field of the axial symmetry, from which one can estimate the values of $g_{||}$ and $g_{\perp}$ as tabulated in Table 3

In relation to $K_2Cr_2O_7$–CF_3COOH system, the following observation may be worthy to note by passing HCl gas into the solution, the ESR signal disappears at an early stage and a doublet with very much reduced intensity appears at a lower field On passing HCl further, one component of the doublet grows up, until eventually the whole spectrum becomes identical with the one due to $CrOCl_4^-$ discussed in the preceding section If one passes dry N_2 gas to drive out the HCl from the solution, the original spectrum characteristic of $K_2Cr_2O_7$–CF_3COOH system can be recovered Thus a reversible conversion between two types of complexes seems to be taking place

(2) *Lactic, citric or tartaric acid plus* $K_2Cr_2O_7$ *in glacial acetic acid* These systems show more or less similar absorptions, of which the ones for citric acid are reproduced

TABLE 3 – g-VALUES OF THE FROZEN SOLUTION (77°K)*

System	$g_{\parallel}$	$g_{\perp}$
CrO_3 in Acetic acid	1 959	1 970
$K_2Cr_2O_7$ in CF_3COOH	1 961	1 977
$K_2Cr_2O_7$ – $(COOH)_2$ in Acetic acid	1 962	1 978

* Uncertainty in measurement ca ± 0 001

in Figs 12 and 13 There are two features immediately noticeable in these results, the line width of the hyperfine component shows a minimum at the second component from the low field end, and the line shapes of the frozen solutions are different from those observed above and appears to be best interpreted as resulting from the crystalline field with rhombic symmetry The g-values along the axes can be estimated by the extension[17] of the method used in the axial field, and are given in Table 4 In Table 5 are summarized the g-values, line widths and the average hyperfine splittings of the solutions at room temperature

DISCUSSION

Examining the g-values obtained here (Table 3) and the ones for the analogous VO-porphyrin complexes[13,18] ($g_{\parallel}$ – 1 947, $g_{\perp}$ = 1 987), one will notice that $g_{\perp}$ is in general greater than $g_{\parallel}$, but the complexes of the type $CrOCl_4$ appear to be

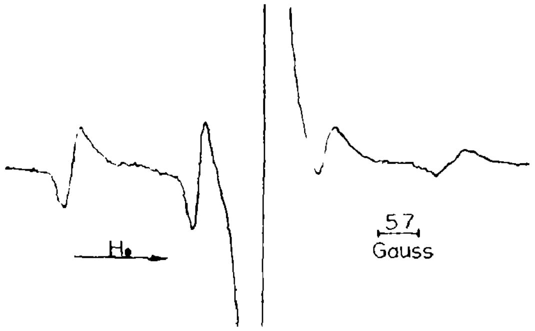


FIG 12 —ESR absorption curve of $K_2Cr_2O_7$–citric acid system at room temperature (Solvent acetic acid)

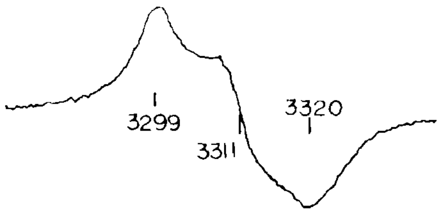


FIG 13 –ESR absorption curve of $K_2Cr_2O_7$–citric acid system frozen at 77°K (Solvent – acetic acid) Field strengths are shown in gauss

TABLE 4 –g-VALUES OF THE FROZEN SOLUTIONS (77°K)*

System	g_1	g_2	g_3
$K_2Cr_2O_7$ + Lactic acid in Acetic acid	1 975	1 979	1 968
$K_2Cr_2O_7$ + Citric acid in Acetic acid	1 973	1 978	1 985

* Uncertainty in measurement ca ±0 001

---

(17) F K KNEUBUHI, *J Chem Phys* **33**, 1074 (1960)

(18) D E O'REILLY, *J Chem Phys* **29**, 1188 (1958)

TABLE 5 —g-VALUES, LINE WIDTHS AND AVERAGE HYPERFINE SPLITTINGS AT ROOM TEMPERATURE*

System	g	Line width (G) $\Delta H_{\max\ \text{slope}}$	Av hf splitting (G)
CrO_3 + Acetic acid	1 9652	2 2	21 0
$K_2Cr_2O_7$ + CF_3COOH	1 9710	1 6	22 0
$K_2Cr_2O_7$ + $(COOH)_2$	1 9779	1 5	18 4
$K_2Cr_2O_7$ + Lactic acid	1 9780	1 5	18 6
$K_2Cr_2O_7$ + Citric acid	1 9781	1 0	18 4

* Accuracy is the same as in Table 1, Solvent = Acetic acid

exceptions In general, if the electric field surrounding the Cr ion is assumed to have a tetragonal symmetry along the z-axis (see Fig 14) the g-values can be calculated by the perturbation theory, taking the spin orbit interaction $(\lambda L\ S)$ into account

$$g_{\parallel} = 2\ 0023\ (1 - 4\lambda/\Delta E_\sigma) \quad \text{and} \quad g_{\perp} = 2\ 0023\ (1 - \lambda/\Delta E_\pi),$$

where ΔE_σ (ΔE_π) is the energy separation between the lowest orbital $(3d_{xy})$ and the excited orbital whose wave function has its maximum in (out of) the xy-plane Given

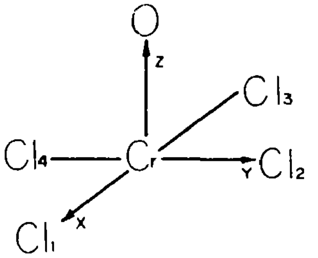


FIG 14 —The structural unit $CrOCl_4$ to show the numbering of Cl ions

the g-values and the excitation energies, the spin orbit interaction constant would be calculated by the equations

Take, for example, the case of $CrOCl_4$, where $g_\perp = 1\ 974$ If the first absorption band at 18,000 cm^{-1} corresponds to the vertical excitation, then λ is calculated to be 230 cm^{-1} *

However, if this value is used in the equation for $g_{\parallel}$, taking into account the fact that the observed $g_{\parallel}$ is practically equal to the free spin value, then ΔE_σ is found to be much higher than seems likely Thus, the ionic model without taking into account the covalency between the Cr ion and the ligands seems to fail to interpret the result in this case

If the molecular orbitals are formed within the hypothetical structural unit CrO^{3+}, using the three $2p$-orbitals of the oxygen atom (in a more rigorous treatment, s-p hybridization should be taken into account) and the $3d$-orbitals of Cr, the situation would not be improved, because it can be shown by the group theory that both $d_{x^2-y^2}$ and d_{xy} can not form a molecular orbital with the oxygen 2p orbitals and, therefore, the expression for $g_{\parallel}$ remains unchanged However, the observed g-values can be better accounted for, if the molecular orbital treatment is extended to the Cl$^-$ ions, and if certain conditions are fulfilled by the bonding parameters.

---

* This is considerably lower than the value by MOORE (383 cm^{-1}) quoted in Reference (4a)

Thus twenty molecular orbitals are constructed from five 3d orbitals of Cr, as the bases for the irreducible representations of the symmetry group C_{4v}. They are

$$4A_1 + A_2 + 3B_1 + 2B_2 + 5E$$

Of the thirty-one electrons in all, thirty p electrons from the ligands are allotted in the following bonding orbitals

$$3A_1 + A_2 + 2B_1 + B_2 + 4E$$

Thus the discussion concerns only the remaining B_2 antibonding orbital which is occupied by the unpaired d-electron, and the excited B_1 and E-orbitals with which the B_2 orbital is coupled through the angular momentum operators

$$\begin{aligned}
\phi(B_1) &= \beta d_{x^2-y^2} + (\beta'/2)(x_1 - y_2 - x_3 + y_4),\\
\phi_1(E) &= \delta d_{yz} - \delta' p_y - \delta''(z_2 - z_4),\\
\phi_2(E) &= -\delta d_{zx} + \delta' p_x + \delta''(z_1 - z_3),\\
\phi(B_2) &= \gamma d_{xy} - (\gamma'/2)(y_1 + x_2 - y_3 - x_4),
\end{aligned}$$

where d and p designate the $3d$-orbitals of Cr ion and $2p$-orbitals of O atom, respectively, and x_i, y_i and z_i stand for $3p_x$, $3p_y$ and $3p_z$ orbitals on the i-th Cl atom, the numbering being shown in Fig. 14.

Using these molecular orbitals, the g-values can be calculated as,

$$\begin{aligned}
g_{\parallel} &= 2.0023\,[1 - (4\lambda/\Delta E_\sigma)\{\beta\gamma + (\beta\gamma' - 2\beta'\gamma)\,S - \beta'\gamma'/2\}^2],\\
g_{\perp} &= 2.0023\,[1 - (\lambda/\Delta E_\pi)\{\gamma\delta + \gamma'\delta''\}^2],
\end{aligned}$$

where S is the overlap integral between the central $d_{x^2-y^2}$ and $3p_x$ (or $3p_y$) on Cl 1 (or 2), and where the hydrogen-like atomic orbitals are adopted. β' and γ' are given by $\beta' = \beta S + \sqrt{(1 - \beta^2)}$ and $\gamma' = \sqrt{(1 - \gamma^2)}$, respectively. The overlap integrals between d_{xy} and ligand orbitals are neglected. Setting, for instance, $\beta = 0.8$, $\gamma = 0.9$ and $S = 0.2$, $g_{\parallel}$ is calculated as,

$$g_{\parallel} = 2.0023\,(1 - 0.34\,\lambda/\Delta E_\sigma)$$

The quantitative aspect of the result should not be taken too literally because of the simplifications adopted in the treatment. In particular, in order to get a more quantitative result, one must use, instead of the simple p- and d-orbitals, the sp hybridized ligand orbitals and the tetragonally hybridized (for ex., dsp^2 or d^2sp^2) orbitals of the Cr ion.

The present result shows that the molecular orbital formation brings the predicted ΔE_σ value to the reasonable range of magnitude, and is indicative of the nature of the bonding in this complex. Thus one can understand the observed g-values of CrOCl_4^- complex by assuming considerable amount of covalency between Cr and Cl. A similar explanation would be applicable to VO-bisacetylacetonate where $g_{\parallel}$ and $g_{\perp}$ are 2.02 and 1.95, respectively.(19)

Acknowledgment—The author is indebted to T. OUCHI for his help in the infra-red absorption measurements.

---

(19) R. D. FELTHAM Thesis (University of California, 1957).

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 945 to 953. Pergamon Press Ltd. Printed in Northern Ireland

ON THE URANATES OF AMMONIUM—II

X-RAY INVESTIGATION OF THE COMPOUNDS IN THE SYSTEM NH_3–UO_3–H_2O

P. C. Debets and B. O. Loopstra
Reactor Centrum Nederland, Petten, Netherlands

(*Received* 12 *November* 1962)

Abstract—The X-ray powder diagrams of four compounds in the system NH_3–UO_3–H_2O have been indexed. The following results were obtained:

I β-$UO_3 \cdot 2H_2O$, orthorhombic, $a = 13.977 \pm 0.004$ Å, $b = 16.696 \pm 0.004$ Å, $c = 14.672 \pm 0.004$ Å

II $3UO_3 \cdot NH_3 \cdot 5H_2O$, orthorhombic, $a = 7.220 \pm 0.003$ Å, $b = 12.198 \pm 0.003$ Å, $c = 15.072 \pm 0.004$ Å

III $2UO_3 \cdot NH_3 \cdot 3H_2O$, hexagonal, $a = 14.087 \pm 0.004$ Å, $c = 14.494 \pm 0.005$ Å,

IV $3UO_3 \cdot 2NH_3 \cdot 4H_2O$, hexagonal, $a = 4.031 \pm 0.004$ Å, $c = 14.58 \pm 0.01$ Å

The structures consist of hexagonal or pseudohexagonal layers of composition $UO_2(O_2)_n$, with the additional O and N atoms of water and ammonia between these layers.

Chemical investigations by Cordfunke(1) show that four well-defined compounds exist in the system NH_3–UO_3–H_2O in equilibrium with aqueous solutions at temperatures up to 50°C. The comparative formulae of these compounds are

I $UO_3 \cdot 2H_2O$
II $3UO_3 \cdot NH_3 \cdot 5H_2O$
III $2UO_3 \cdot NH_3 \cdot 3H_2O$
IV $3UO_3 \cdot 2NH_3 \cdot 4H_2O$

Compound I is by far the best known of this series. Its X-ray diagram has been obtained both from synthetic products(2,3) and from samples of mineral origin.(4) The patterns of the natural substances are very similar to those of the synthetic ones, but they are not identical.

Substances with the unit cell of our compound II have been mentioned in the literature under a variety of chemical compositions and are commonly referred to as A.D.U. (ammonium diuranate). An X-ray diagram of this compound has been published by Garner.(5)

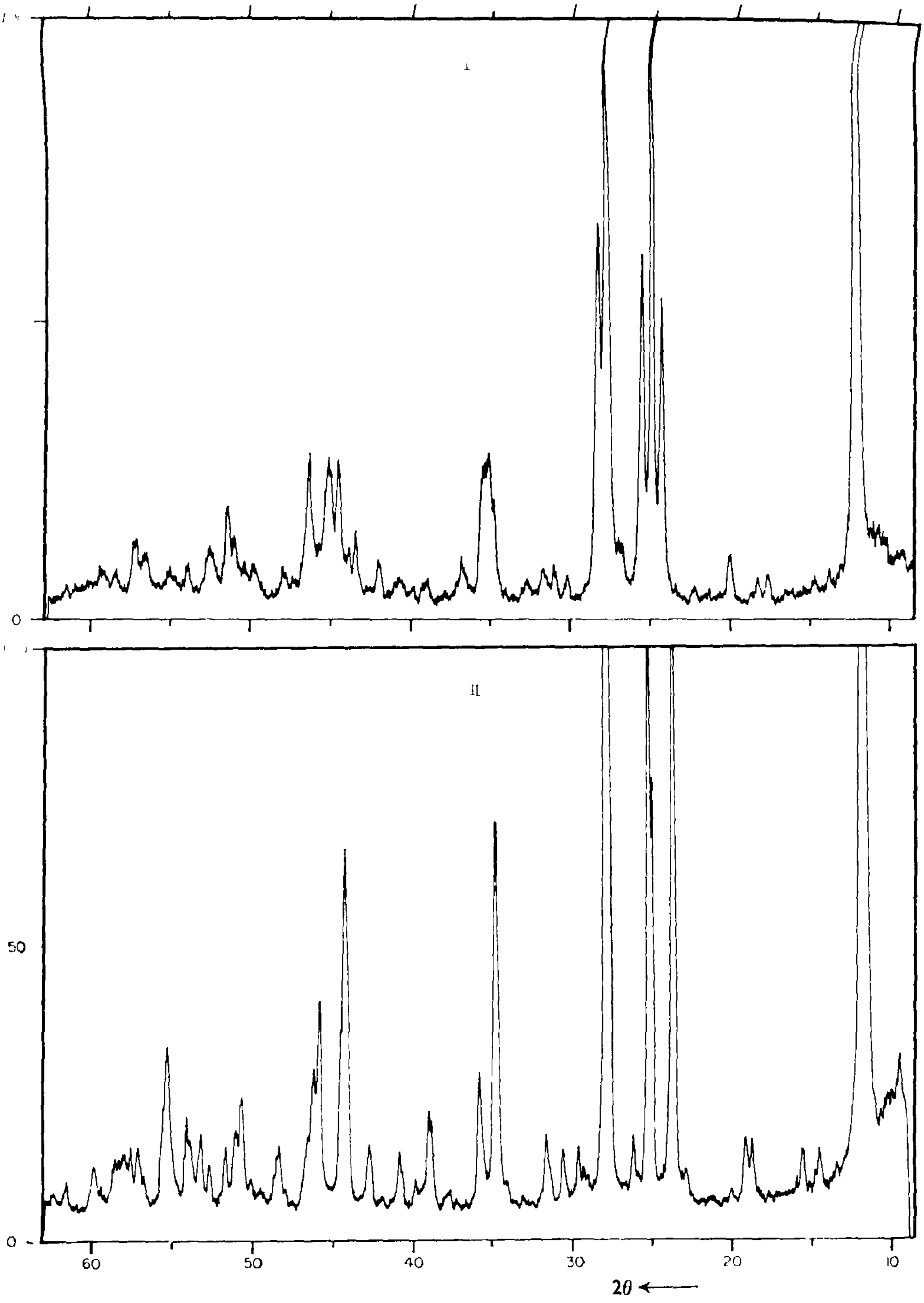
For both substances, our data are more complete and somewhat more accurate than those quoted above. In the case of compound II we have moreover been able to work with a chemically pure compound prepared by Cordfunke.(1) For these reasons we have listed the diagrams of these compounds here together with those of compounds III and IV, the patterns of which have not been published yet.

---

(1) E. H. P. Cordfunke, *J. Inorg. Nucl. Chem.* **24**, 303 (1962), I in this series.
(2) J. K. Dawson *et al.*, *J. Chem. Soc.* 3531 (1956).
(3) H. W. Dunn, ORNL-2092 (1956).
(4) C. L. Christ and J. R. Clark, *Amer. Mineral.* **45**, 1026 (1960).
(5) E. V. Garner, *J. Inorg. Nucl. Chem.* **21**, 380 (1962).

EXPERIMENTAL

The samples were obtained as microcrystalline powders the crystallinity of which was brought to an optimum by shaking the reaction mixture for several weeks to months in a thermostated bath. The diagrams shown in Fig. 1 were recorded on a Philips diffractometer using Ni-filtered Cu radiation.



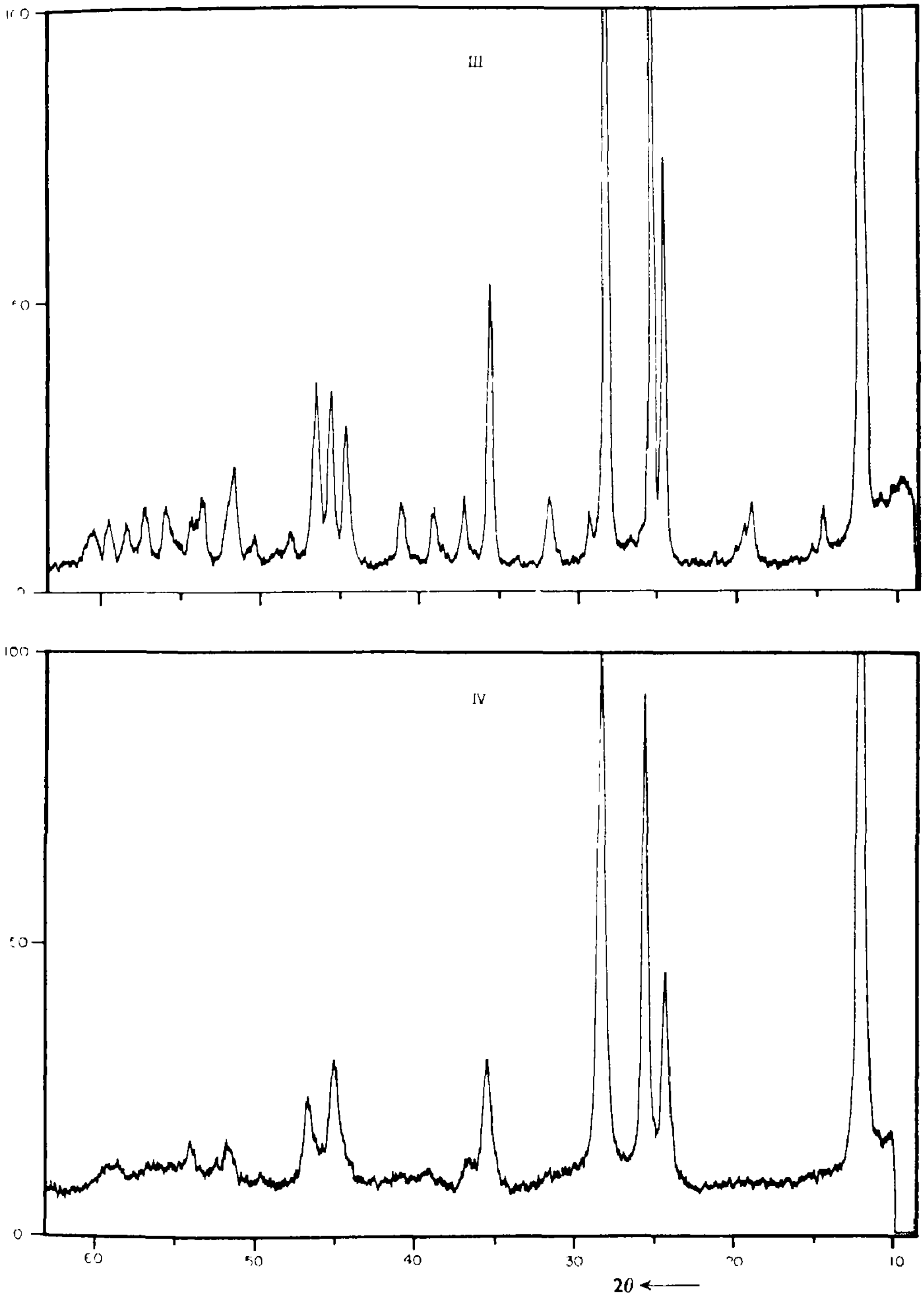


FIG. 1.—The X-ray diagrams of the four compounds (CuKα-radiation)

RESULTS AND DISCUSSION

The diffraction patterns of the compounds I, II, III and IV are listed in Tables 1, 2, 3 and 4, respectively. $\sin^2\theta$ values in Tables 1 and 2 have been calculated for $CuK\alpha_1$-radiation with $\lambda = 1.5405$ Å, in Tables 3 and 4 for $CuK\alpha$, with $\lambda = 1.5418$ Å, because the α_1–α_2 doublet was not resolved in the poorly crystalline products III and IV.

Table 5 contains the edges a, b and c of the unit cells, the symmetry of the unit cells, the number Z of uranium atoms per unit cell, the edges a', b', c' and the angle γ' between a' and b' of the subcells on which the stronger reflexions can be indexed, and the volume V' of these subcells. The cell dimensions were refined on an Electrologica X_1 computer by means of a least squares programme.

The crystallinity of the products decreases markedly with increasing ammonia content. In product IV the line broadening becomes so serious as to obscure any reflection except those due to the subcell. Moreover in contact with moist air, part of the ammonia in this product is exchanged for water.(1) This causes a rapid change of the positions of the reflexions over up to 0.5 degree. For these reasons the values given for this compound are less accurate than those for the others.

As can be seen from Fig. 1, the strong reflections from the four products are very closely related. This can be traced to the existence of sublattices which are almost identical in the various compounds. The existence of hexagonal or pseudohexagonal subcells in hydrated compounds of hexavalent uranium has been noted by several investigators.(4,5,6) They are formed by the uranium atoms, which are approximately situated on the corners of the subcells.

The subcell-reflexions in Tables 1, 2, and 3 are printed in italics, in Table 5 the subcells are indicated with primed cell constants. The idealized subcell is sketched in Fig. 2.

Each uranium atom is surrounded by eight oxygen atoms on the corners of a deformed cube compressed along the body diagonal which coincides with the c'-axis of the subcell. These cubes, sharing edges, form layers perpendicular to the c'-axis, essentially identical to those in α-UO_3.(7) The average composition of these layers, apart from the hydrogen atoms, is $UO_2(O_2)$. The two short (~2.0 Å) U–O bonds along the c'-axis form the uranyl group, the other U–O distances are 2.4 to 2.5 Å as deduced from spatial considerations.

From the shape and similarity of the uranium sublattices several conclusions can be drawn about the chemical composition and the structure of these compounds. In the first place it is evident from the volume of the subcells that the ammonia compounds are formed by substitution of water by ammonia such that per uranium atom there are always 2-x water molecules and x ammonia molecules. This has been the guiding principle throughout the chemical investigations.(1) Secondly, the formula $UO_3 \cdot 2H_2O$ cannot be the correct one; $H_2UO_4 \cdot H_2O$ seems more nearly appropriate. Apparently the U—O bonds are not broken during the formation of the ammonia compounds. The highest member of the series UO_3-H_2O-NH_3 would therefore seem to be $NH_4 \cdot H \cdot UO_4$, corresponding to ammonium diuranate. Ironically, this compound was not obtained.

(6) E. A. Ippolitova and L. M. Kovba, *Dokl. Akad. Nauk SSSR*, **138**, 377 (1961).

(7) W. H. Zachariasen, *Acta Cryst.* **1**, 265 (1948).

Table 1.—Diffraction pattern of compound 1. $\sin^2\theta$ calculated with λ = 1.5405 Å ($CuK\alpha_1$)

$\sin^2\theta$ × 10^4 (obs)	$\sin^2\theta$ × 10^4 (calc)	*hkl*	*I*	$\sin^2\theta$ × 10^4 (obs)	$\sin^2\theta$ × 10^4 (calc)	*hkl*	*I*	$\sin^2\theta$ × 10^4 (obs)	$\sin^2\theta$ × 10^4 (calc)	*hkl*	*I*
79.4	79.2	111	2	1044.6	1043.8	116	1	*2226.0*	*2225.8*	*248*	2
85.6	85.2	020	1	1114.9	1114.6	610	2	*2246.8*	*2249.7*	*408*	2
110.5	*110.2*	*002*	100	1154.0	1153.8	335	2	2278.2	2277.0	636	2
143.1	143.1	121	1	1197.4	1196.2	415	2		2277.4	2 10 1	
161.8	161.9	112	2		1198.8	533		*2289.3*	*2289.1*	*484*	3
195.4	195.4	022	1		1198.8	226		*2356.1*	*2354.3*	*086*	1
206.2	206.6	220	<1	1224.7	1224.8	612	1	*2384.4*	*2384.7*	*804*	2
234.0	234.1	221	2	1251.7	1251.4	155	1	*2424.1*	*2426.0*	*646*	2
250.0	249.5	131	1	1280.2	1279.6	461	3	2497.0	2497.8	2 10 3	1
299.3	299.7	113	5	1322.0	1321.3	173	1	2532	2532.2	843	1
317.0	316.9	222	1	*1363.1*	*1362.2*	*080*	2	2573	2572.6	921	1
322.2	322.2	311	1	1389.8	1389.8	081	3		2576.2	834	
340.5	340.5	040	1	*1433.8*	*1433.9*	*640*	7	2599	2599.7	1 10 4	1
368.4	368.1	041	1	*1454.7*	*1454.2*	*246*	5	2654	2655.4	922	<1
404.7	404.8	312	1	*1472.6*	*1472.4*	*082*	2	2695	2695.3	764	<1
441.1	*441.0*	*004*	25	*1477.6*	*1478.1*	*406*	4	2713	2714.6	538	<1
462.1	*462.0*	*240*	40	1500.0	1499.3	416	1	2735	2737.4	861	<1
468.4	468.7	322	5		1500.1	463		2795	2793.2	923	<1
486.3	*485.9*	*400*	20	*1544.5*	*1544.1*	*642*	9	*2835*	*2840.5*	*486*	1
489.4	489.6	241	10	1610.4	1610.2	083	1	*2937*	*2935.9*	*806*	1
535.0	534.8	411	2	1638.2	1639.1	472	1	2954	2957.2	816	1
542.5	542.7	313	1	1652.0	1652.9	651	1	3012	3015.6	468	<1
572.1	*572.2*	*242*	50	1683.0	1681.9	643	1	3054	3055.2	4 10 4	<1
595.8	*596.1*	*402*	25	1734.2	1732.8	554	1	3086	3085.9	10 1 1	<1
677.4	677.4	430	1	*1762.3*	*1763.8*	*008*	2	3166	3168.3	10 1 2	<1
710.6	710.0	243	4	*1802.9*	*1803.1*	*084*	2	*3210*	*3197.7*	*648*	2
739.6	740.7	115	3	1813.1	1812.4	247	1		*3218.0*	*2 4 10*	
754.7	754.0	234	1	*1846.4*	*1848.0*	*480*	2	*3244*	*3241.9*	*4 0 10*	1
	755.2	413		*1874.9*	*1874.8*	*644*	7	*3301*	*3296.5*	*2 12 2*	1
793.5	793.7	061	2	1922.8	1921.5	427	1		*3305.8*	*8 8 0*	
833.5	833.0	351	1	*1943.0*	*1943.7*	*800*	2	3327	3328.5	5 10 4	<1
855.3	854.0	441	1	*1956.8*	*1958.3*	*482*	3	*3374*	*3377.5*	*10 4 0*	1
887.7	887.6	260	1	1990.9	1992.5	811	1	*3412*	*3416.1*	*8 8 2*	1
903.2	*902.9*	*244*	15	2003.5	2002.3	193	1	*3485*	*3487.8*	*10 4 2*	1
927.4	*926.9*	*404*	8	*2053.4*	*2053.8*	*802*	2	3552	3550.7	4 12 0	1
979.1	978.3	531	1	2097.2	2096.1	483	1	*3609*	*3611.8*	*4 8 8*	1
992.3	*992.2*	*006*	2	2132.1	2131.0	517	1	*3629*	*3627.2*	*2 12 4*	1
1013.1	1012.1	424	1	2163.6	2162.8	813	1	*3743*	*3746.8*	*8 8 4*	1
	1013.5	016			2163.8	671		*3818*	*3818.5*	*10 4 4*	1

TABLE 2 —DIFFRACTION PATTERN OF COMPOUND II, $\sin^2\theta$ CALCULATED WITH λ = 1 5405 Å (CuKα_1)

$\sin^2\theta \times 10^4$ (obs)	$\sin^2\theta \times 10^4$ (calc)	*hkl*	*I*	$\sin^2\theta \times 10^4$ (obs)	$\sin^2\theta \times 10^4$ (calc)	*hkl*	*I*	$\sin^2\theta \times 10^4$ (obs)	$\sin^2\theta \times 10^4$ (calc)	*hkl*	*I*
66 1	66 0	011	1	1157 4	1158 1	215	1	*2317 9*	*2318 7*	*264*	2
104 6	*104 5*	*002*	100	1208 3	1207 8	242	2	*2345 5*	*2346 0*	336	2
156 4	156 2	110	1	1217 3	1217 7	152	3	*2375 6*	*2375 8*	*066*	1
159 6	159 5	020	2	1233 4	1232 5	321	1	2389 7	2391 4	129	2
182 7	182 3	111	3	1278 1	1277 7	225	1	2438 9	2438 5	424	1
261 1	260 7	112	1	1319 9	1319 7	017	4	2461 6	2461 7	354	1
264 0	264 0	022	3	1348 4	1348 3	153	1	2486 0	2486 1	327	3
275 1	274 9	013	4	*1406 2*	*1405 5*	*206*	14	*2612*	*2611 8*	*0 0 10*	1
	275 8	120			*1405 7*	*330*		2653	2656 6	082	1
302 3	301 9	121	1	*1415 3*	*1415 5*	*136*	15	2668	2668 4	180	1
390 5	391 3	113	2	*1436 0*	*1435 6*	*060*	4		2668 5	058	
418 3	*417 9*	*004*	70	*1510 1*	*1510 2*	*332*	8	2692	2694 6	181	1
465 3	*465 3*	*200*	25	1530 4	1531 1	154	2	2736	2734 2	443	1
475 3	*475 2*	*130*	50	*1539 8*	*1540 0*	*062*	5	2779	2774 8	248	1
510 7	510 9	123	3	1555 5	1555 6	127	2		2784 8	158	
532 2	531 3	211	1	1564 2	1565 0	226	2	*2800*	*2801 3*	*406*	1
	534 2	104		1577 7	1578 0	161	1	*2842*	*2841 1*	*266*	1
569 3	*569 7*	*202*	40		1578 3	046		2961	2960 8	426	1
579 3	*579 7*	*132*	70	1650 0	1649 9	055	1	2974	2970 0	084	1
624 9	624 8	220	1	*1671 2*	*1671 6*	*008*	4		2970 7	0 3 10	
638 1	638 0	040	1	1696 2	1694 6	146	1	3010	3010 5	176	2
651 1	650 9	221	3		1697 3	253		*3076*	*3077 1*	*2 0 10*	3
692 6	692 8	015	4	1739 7	1739 7	315	1		*3077 3*	*338*	
	693 7	124		1763 2	1764 4	236	1	*3086*	*3087 0*	*1 3 10*	1
729 5	729 2	222	2	1784 6	1784 9	217	1	*3105*	*3107 1*	*068*	2
743 1	742 5	042	4	*1824 1*	*1823 6*	*334*	7	3181	3180 6	267	1
809 4	809 1	115	1	*1853 3*	*1853 4*	*064*	2		3182 8	513	
859 7	858 8	142	1	*1861 1*	*1861 1*	*400*	3	3235	3236 6	2 2 10	1
	859 8	223		*1901 0*	*1900 8*	*260*	3	*3267*	*3266 8*	*530*	1
883 9	883 2	*204*	9	*1966 0*	*1965 5*	*402*	3	*3297*	*3296 6*	*460*	1
893 4	*893 1*	*134*	25	*2005 2*	*2005 3*	*262*	4	3323	3322 7	461	1
928 4	928 6	232	2	2043 9	2043 5	246	3	*3370*	*3371 3*	*532*	1
	928 8	125			2043 8	350		*3401*	*3401 1*	*462*	1
940 0	*940 2*	*006*	9	2053 9	2053 5	156	2	3419	3418 7	374	1
1022 7	1023 0	051	1	2068 4	2069 9	351	4	3435	3439 3	446	1
1042 6	1042 7	224	1		2070 3	170		*3451*	*3450 9*	*192*	<1
1056 3	1055 9	044	1	2115 1	2115 1	255	1	*3531*	*3532 6*	*408*	<1
	1056 6	106		2125 2	2125 0	422	1	*3574*	*3572 4*	*268*	2
1103 6	1103 3	240	4	*2136 3*	*2136 8*	*208*	3	*3686*	*3684 7*	*534*	1
1112 9	1112 8	311	4	*2147 4*	*2146 8*	*138*	9	*3715*	*3714 5*	*464*	2
	1113 2	150		2173 4	2174 8	172	3	3742	3741 8	178	1

TABLE 3 —DIFFRACTION PATTERN OF COMPOUND III $\sin^2\theta$ CALCULATED WITH λ = 1 5418 Å (CuKα)

$\sin^2\theta \times 10^4$ (obs)	$\sin^2\theta \times 10^4$ (calc)	*hkil*		$\sin^2\theta \times 10^4$ (obs)	$\sin^2\theta \times 10^4$ (calc)	*hkil*	*I*	$\sin^2\theta \times 10^4$ (obs)	$\sin^2\theta \times 10^4$ (calc)	*hkil*	*I*
68 4	68 2	$10\bar{1}1$	1	1116 2	1118 0	$42\bar{6}0$	3	2448 4	2449 2	$40\bar{4}8$	1
113 0	*113 2*	*0002*	100	1229 2	1226 3	$31\bar{4}5$	4	*2456 9*	*2455 7*	$60\bar{6}6$	2
160 3	159 7	$20\bar{2}0$	3		1231 1	$42\bar{6}2$		2531	2528 9	$62\bar{8}4$	2
274 1	272 9	$20\bar{2}2$	3	*1437 9*	*1437 4*	$60\bar{6}0$	10	*2932*	2928 3	$42\bar{6}8$	1
295 0	294 4	$10\bar{1}3$	2	*1498 5*	*1497 5*	$22\bar{4}6$	10		*2934 8*	$44\bar{8}6$	
451 1	452 6	*0004*	22	*1551 6*	*1550 5*	$60\bar{6}2$	11	3033	3034 5	$6\,4\,\overline{10}\,2$	1
479 2	*479 1*	$22\bar{4}0$	60	1659 7	1657 2	$40\bar{4}6$	2	3098	3094 6	$62\bar{8}6$	1
534 5	534 1	$21\bar{3}3$	1	*1808 8*	*1810 5*	*0008*	1	3148	3147 6	$6\,4\,\overline{10}\,2$	1
591 9	*592 3*	$22\bar{4}2$	70	*1889 6*	*1890 0*	$60\bar{6}4$	5	*3245*	*3247 8*	$60\bar{6}8$	1
638 6	638 9	$40\bar{4}0$	3	*1916 3*	*1916 5*	$44\bar{8}0$	3	*3309*	*3307 9*	$2\,2\,\bar{4}\,10$	1
750 8	752 0	$40\bar{4}2$	4	*2030 0*	*2029 6*	$44\bar{8}2$	4	*3357*	*3353 9*	$8\,2\,\overline{10}\,0$	1
930 9	*931 8*	$22\bar{4}4$	18	2076 2	2076 2	$62\bar{8}0$	2	*3470*	*3467 1*	$8\,2\,\overline{10}\,2$	2
987 7	986 5	$21\bar{3}5$	1	2135 9	2136 3	$42\bar{6}6$	1		3467 7	$4\,0\,\bar{4}\,10$	
1017 6	*1018 3*	*0006*	3	2186 9	2189 4	$62\bar{8}2$	3	*3721*	*3726 9*	$44\bar{8}8$	1
1092 9	1091 4	$40\bar{4}4$	1	*2290 3*	*2289 6*	$22\bar{4}8$	3	*3804*	*3806 5*	$8\,2\,\overline{10}\,4$	1
	1093 0	$41\bar{5}3$		*2368 4*	*2369 1*	$44\bar{8}4$	2				

TABLE 4 —DIFFRACTION PATTERN OF COMPOUND IV, $\sin^2\theta$ CALCULATED WITH λ = 1 5418 Å (CuKα)

$\sin^2\theta \times 10^4$ (obs)	$\sin^2\theta \times 10^4$ (calc)	*hkil*	*I*	$\sin^2\theta \times 10^4$ (obs)	$\sin^2\theta \times 10^4$ (calc)	*hkil*	*I*	$\sin^2\theta \times 10^4$ (obs)	$\sin^2\theta \times 10^4$ (calc)	*hkil*	*I*
111 1	111 9	0002	100	1495 4	1494 8	$10\bar{1}6$	4	2397	2398 4	$20\bar{2}4$	1
448 4	447 6	0004	15	1573 7	1575 1	$11\bar{2}2$	5	2470	2470 2	$11\bar{2}6$	1
488 2	487 7	$10\bar{1}0$	40	1794 4	1790 3	0008	1	2955	2957 9	$20\bar{2}6$	1
597 6	599 4	$10\bar{1}2$	45	1909 7	1910 7	$11\bar{2}4$	2	3251	3253 4	$11\bar{2}8$	1
933 3	935 3	$10\bar{1}4$	6	1951 0	1950 9	$20\bar{2}0$	2	3289	3284 9	$1\,0\,\bar{1}\,10$	1
1006 8	1007 0	0006	1	2063	2062 8	$20\bar{2}2$	3	3524	3525 9	$21\bar{3}2$	1
1462 3	1463 2	$11\bar{2}0$	5	2278	2277 9	$10\bar{1}8$	1	3866	3861 6	$21\bar{3}4$	1

TABLE 5. SUMMARIZED DATA ON THE UNIT CELLS AND SUBCELLS (PRIMED VALUES) OF THE COMPOUNDS I, II, III AND IV

Compound	I	II	III	IV
a	(13.977 ± 0.004) Å	(7.220 ± 0.003) Å	(14.087 ± 0.004) Å	(4.031 ± 0.004) Å
b	(16.696 ± 0.004) Å	(12.198 ± 0.003) Å		
c	(14.672 ± 0.004) Å	(15.072 ± 0.004) Å	(14.494 ± 0.005) Å	(14.58 ± 0.01) Å
Symmetry	Orthorhombic	Orthorhombic	Hexagonal	Hexagonal
Z	32	12	24	2
a'	(4.070 ± 0.002) Å	(4.143 ± 0.002) Å	(4.066 ± 0.001) Å	(4.031 ± 0.004) Å
b'	(4.174 ± 0.002) Å	(4.066 ± 0.002) Å		
c'	(7.336 ± 0.002) Å	(7.536 ± 0.002) Å	(7.247 ± 0.002) Å	(7.288 ± 0.007) Å
γ'	120° 51′ ± 1′	119° 23′ ± 1′	120°	120°
V'	(107.0 ± 0.1) Å³	(110.6 ± 0.1) Å³	(103.8 ± 0.1) Å³	(102.5 ± 0.2) Å³

The formula $H_2UO_4 \cdot H_2O$ is in agreement with results by DEANE⁽⁸⁾ from infra-red investigations. We do not support his conclusion that the ammonia molecule is directly linked to the uranium atom. Proton magnetic resonance work by PORTE *et al.*⁽⁹⁾ leads to a formula $H_2U_2O_7 \cdot 3H_2O$. From the X-ray data alone it seems hardly feasible to obtain a definite answer to the question whether this description is the correct one. As we intend to collect additional data on these compounds by neutron

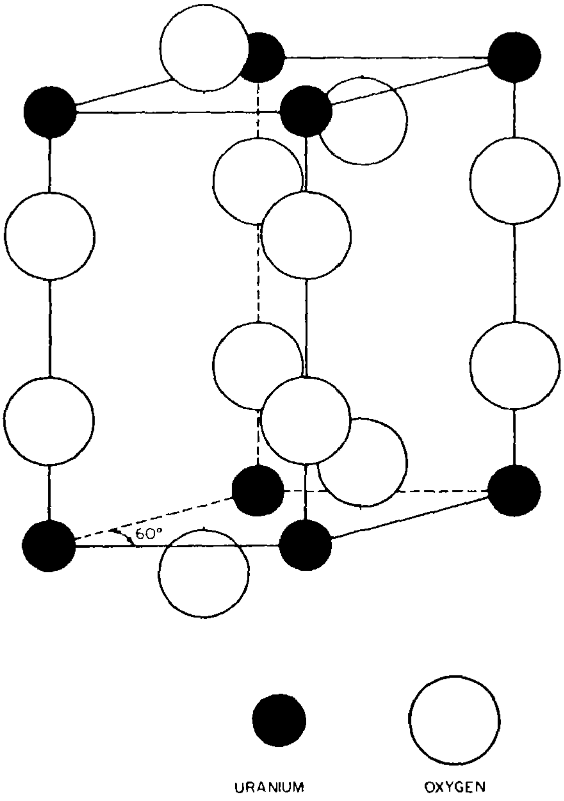


FIG. 2.—The idealized subcell.

⁽⁸⁾ A. M. DEANE, *J. Inorg. Nucl. Chem.* **21**, 238 (1962).

⁽⁹⁾ A. L. PORTE, H. S. GUTOWSKI and J. E. BOGGS, *J. Chem. Phys.* **36**, 1695 (1962).

diffraction we have not yet tried to work out the X-ray intensities to full detail Judging from the large unit cell of product I it would be attractive to describe this compound with units containing more than one uranium atom

In the products I, II and III the c-axis of the unit cell is twice the axis c' of the subcell In these products space group considerations make it probable that there is a symmetry plane between the layers This is confirmed by the space groups derived by CHRIST and CLARK(1) for their mineral samples It is reasonable to assume that this symmetry plane is also present in compound IV, because of the very striking similarity between the products in general This assumption is not substantiated by the X-ray diagram but as mentioned above this may well be due to the poor crystallinity of the product The number of nitrogen atoms in the resulting unit cell is $\frac{4}{3}$ Unless the cell volume has to be tripled, this would indicate that in this compound the water and ammonia groups are distributed in a statistical way

It has not been possible to establish unequivocally the space groups of the compounds Next to the subcell reflections there are only rather few others of moderate or small intensity Furthermore, the large unit cell does not always allow a unique indexing of these, which should be the relevant ones in the space group determination Although many groups can be ruled out with some degree of certainty on account of the indices which are found and by making some assumptions about the structure of the $UO_2(O_2)$ layers, a final selection of the space group was not obtained The possible groups for product I also include those derived by CHRIST and CLARK(5) from single crystals of schoepite, which is a mineral form of compound I

Note added in proof Since the completion of this paper we have been informed by G KORILLVL and P M DE WOLFF (Technical University, Delft) that the most probable space group for UO_3 $2H_2O$ is Pbna, as derived from X-ray data obtained with a modified Guinier-de Wolff camera

This would be in complete agreement with CHRIST and CLARK (4)

Acknowledgements The authors wish to express their gratitude to Dr E H P CORDFUNKE for providing the specimens and for many valuable discussions and to Mr H P SIRUCH for his help in the computer programming and calculations

EXPERIMENTAL

HDPM was prepared as previously described(1) and TOPO was an Eastman Kodak white-label product. 1,2-Dichlorobenzene was used as the diluent for HDPM and TOPO in all extraction studies. Stock uranium (VI) solutions were prepared from U_3O_8 according to the method of BROUNS and MILLS(4) or from Ames Laboratory uranium metal.

Partition studies were made by equilibrating equal volumes (usually 10 or 20 ml) of aqueous and organic solutions of known composition by shaking them in glass separatory funnels fitted with Teflon stopcocks. Equilibrium conditions were reached very rapidly when 1,2-dichlorobenzene solutions of HDPM were equilibrated with mineral acid solutions of uranium (VI) and a 10 min shaking period was arbitrarily selected. The partition experiments were made at ambient room temperature of 25 ± 2°C. Aliquot samples of the uranium-poor phase were taken for analysis.

Uranium was determined in the aqueous phase if $D > 1$ or in the organic phase after stripping with Na_2CO_3 if $D < 1$. The arsenazo method(5) was used for the determination when $D > 1$ and the peroxide method(6) when $D < 1$.

The amount of acid extracted was determined by titration of an aliquot of the organic phase with 0.05 N tetrabutyl ammonium hydroxide using methylene blue indicator.

Ostwald-Fenske type viscometers thermostated at 25.00 ± 0.01°C were used to measure the capillary flow of the solvent and uranium (VI) nitrate complexes with HDPM and TOPO. A capillary was chosen so that the efflux time was always between 100 and 500 sec. The efflux time of each solution was measured three times; the precision was within 0.5 sec.

Visible spectra were obtained with the Cary Model 14 recording spectrophotometer. Spectrophotometric analyses were made with the Beckman Model DU spectrophotometer.

RESULTS AND DISCUSSION

Effect of solvent

Cyclohexane has been consistently used as a diluent for TOPO.(3) When a cyclohexane solution of HDPM was equilibrated with uranium (VI) in 1 M nitric acid, quantitative extraction was observed. When a sufficiently large amount of uranium was extracted, a sticky, yellow, viscous third phase was formed which was more dense than the cyclohexane phase and appeared to contain nearly all of the uranium. This did not occur when TOPO was used as the extractant. The viscous nature of this substance suggested that it might be polymeric.

The polymeric-like substance was formed when other nonpolar solvents such as *p*-cymene, tetrahydronaphthalene, benzene, or toluene were used as diluents for HDPM. When carbon tetrachloride was used as a diluent, a polymeric-like substance was also formed; however, unlike the other non-polar solvents mentioned, a two-phase system was obtained upon prolonged shaking. Third phase formation was not observed when 1-nitropropane, 1-chloronitropropane, methylenechloride, chloroform, 1,2-dichlorobenzene, methylisobutyl ketone or a 1:1 mixture of the latter with cyclohexane were used as diluents for HDPM. 1,2-Dichlorobenzene was chosen as the diluent because of its good stability and appropriate density.

Comparative viscosity measurements of uranium-saturated solutions of HDPM and TOPO in 1,2-dichlorobenzene showed only slight differences in the limiting viscosity number. When carbon tetrachloride was used as the diluent, however, the HDPM–uranium solutions had much higher viscosities than the TOPO–uranium solutions thus indicating polymer formation in the former case. The viscosity of the

(4) R. J. BROUNS and W. W. MILLS, Report *HW*-39767 (1955).

(5) J. S. FRITZ and M. JOHNSON-RICHARD, *Analyt. Chim. Acta* **20**, 164 (1959).

(6) E. B. SANDELL, *Colorimetric Determination of Traces of Metals*, (3rd Ed.), Interscience, New York (1959).

solutions when cyclohexane was used as the diluent were too high to be measured with the Ostwald capillaries in the case of the HDPM-uranium system

The viscosity number, η_c was calculated from the viscosity of the solution, η, the viscosity of the solvent, η_0, and the concentration of the complex, c, in g/ml by the following equation

$$\eta_c = \frac{\eta - \eta_0}{\eta_0 c}$$

The limiting viscosity number, $[\eta]$, is obtained by extrapolation of the viscosity number to zero concentration

$$[\eta] = \lim_{c \to 0} \eta_c = \lim_{c \to 0} \frac{1}{c} \ln \frac{\eta}{\eta_0}$$

The limiting viscosity number is related to the molecular weight of the polymer by the equation,

$$[\eta] = KM^a,$$

where K and a are dependent upon the properties of the solvent and solute molecules and their interactions One can calculate an approximate value for the ratio of the molecular weights of the polymers in the two systems,

$$\frac{[\eta]_{\text{HDPM}}}{[\eta]_{\text{TOPO}}} = \frac{K'(M')^a}{K''(M'')^a} = \left(\frac{M'}{M''}\right)^a,$$

where K' and K'' are assumed to be equal and a is taken to be 0 7 From this relationship, it was estimated that the molecular weight of the HDPM complex with uranium is approximately eighty times that of the TOPO complex Polymer formation was also observed with other metals when non-polar solvents were used as diluents for HDPM

Extraction of mineral acids

The extraction of the mineral acids into a 0 05 M solution of HDPM in 1,2-dichlorobenzene is shown in Fig 1 along with the data obtained by WHITE and ROSS[(3)] for the extraction of these acids into a 0 1 M solution of TOPO in cyclohexane The distribution behaviour of the various acids into HDPM is seen to be very similar to their behaviour with TOPO As with TOPO, the acids fall into two groups with nitric and perchloric acids having a different slope than hydrochloric and sulphuric acids at low acid concentrations Only in the case of nitric acid, however, did the mole ratio of acid to HDPM exceed two although, at higher concentrations it is greater than one for all the acids

The equilibrium constant for the reaction,

$$Y_{(o)} + H^+_{(a)} + NO_3^-{}_{(a)} \rightarrow Y\,HNO_{3(o)}$$

is given by Equation (1),

$$K_1 = \frac{[Y\,HNO_3]}{[H][NO_3][Y]} = \frac{D_H}{[NO_3][Y]}, \tag{1}$$

where Y = HDPM or TOPO and [] signify equilibrium molar concentrations Ionic charges have been omitted from equilibrium expressions for greater clarity Equilibrium constants were determined by equilibrating varying concentrations of organic ligand with 1 M HNO_3 The ratio of acid extracted to organic ligand was less than

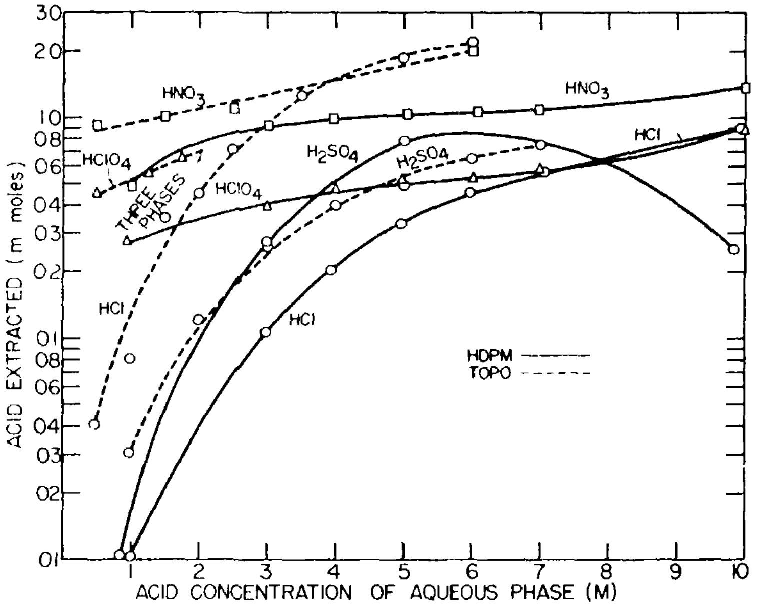


FIG. 1. Extraction of mineral acids as a function of acid concentration with HDPM and TOPO

Data on TOPO (dotted lines) from WHITE and ROSS[1] Organic phase 10 ml 0.05 M HDPM in 1,2-dichlorobenzene Phase ratio 1 Extraction time = 10 min

TABLE 1. K_1 FOR THE EXTRACTION OF 1 M HNO_3 BY HDPM AND TOPO

$[HDPM]_i$*	D_H	$\frac{[Y \cdot HNO_3]}{[HDPM]_i}$	K_1	$[TOPO]_i$	D_H	$\frac{[Y \cdot HNO_3]}{[TOPO]_i}$	K_1
5×10^{-2}	0.04795	0.909	11.1	1×10^{-1}	0.1028	0.923	14.9
2×10^{-2}	0.01928	0.940	16.7	5×10^{-2}	0.0464	0.879	8.1
1×10^{-2}	0.00965	0.949	19.3	1×10^{-2}	0.00928	0.910	10.6
5×10^{-3}	0.00477	0.943	17.1	5×10^{-3}	0.00443	0.874	7.1
2.5×10^{-3}	0.00232	0.921	11.9			Ave	10.2
		Ave =	15.2				

* Subscript i denotes initial concentration

one in all cases and thus the presence of a 1 : 1 species was indicated. Equilibrium constants were then calculated for the reaction of 1 M nitric acid with HDPM and TOPO (Table 1). The values for α, the fraction of uncomplexed ligand, were then calculated from Equation (2)

$$\alpha^{-1}_{Y(H)} = 1 + K_1[H][NO_3]$$

$$\alpha_{HDPM(H)} = 0.062$$

$$\alpha_{TOPO(H)} = 0.089$$

Complexes of HDPM *with uranium (VI) nitrate*

Previous workers(3, 7) have shown by loading capacity studies that two neutral ligands such as tributyl phosphate, TBP, or TOPO combine with each uranium (VI)

---

(7) W. B. WRIGHT, JR., Report Y-838, (1952).

ion. However, similar studies of the HDPM–uranium (VI) system in 1,2-dichlorobenzene indicate the presence of a 1:1 species, while in the presence of excess HDPM, a 2:1 species is most consistent with the extraction data. If the following over-all reaction describes the extraction of uranium (VI) in the presence of excess extractant, the expression for the over-all equilibrium constant is given by Equation (3)

$$\mathrm{UO}_{2(a)}^{2+} + 2\mathrm{NO}_{3(a)}^{-} + 2\mathrm{Y}_{(o)} \rightarrow \mathrm{UO}_2(\mathrm{NO}_3)_2 \cdot 2\mathrm{Y}_{(o)}$$

$$\mathrm{K}_2 = \frac{[\mathrm{UO}_2(\mathrm{NO}_3)_2 \cdot 2\mathrm{Y}]\gamma_c}{[\mathrm{UO}_2][\mathrm{NO}_3]^2\gamma_{\pm}{}^3[\mathrm{Y}]^2\gamma_{\mathrm{Y}}{}^2} \tag{3}$$

The symbols γ_c, γ_{Y}, and $\gamma_{\pm}$ are the activity coefficients of the extracted complex, the extractant, and the mean activity coefficient for uranium (VI) nitrate in the aqueous phase. The equilibrium expression in Equation 3 can be rearranged as shown in Equation (4),

$$K_2' = \frac{K_2\gamma_{\pm}{}^3\gamma_{\mathrm{Y}}{}^2\alpha^2\beta}{\gamma_c} = \frac{D_{\mathrm{U}}}{[\mathrm{Y}']^2[\mathrm{NO}_3]^2}$$

$$= \frac{D_{\mathrm{U}}}{\{[\mathrm{Y}]_i - 2[\mathrm{UO}_2(\mathrm{NO}_3)_2 \cdot 2\mathrm{Y}]\}^2[\mathrm{NO}_3]^2}, \tag{4}$$

where $\alpha = [\mathrm{Y}]/[\mathrm{Y}']$, $\beta = [\mathrm{UO}_2]/[\mathrm{UO}_2']$, $[\mathrm{Y}']$ and $[\mathrm{UO}_2']$ are total concentrations not bound to the metal or ligand, respectively, and $[\mathrm{Y}]_i$ = initial molar concentration. For a series of extractions in which the nitric acid and uranium concentrations are held constant, the slope of a plot of log $D_{\mathrm{U}}/[\mathrm{NO}_3^-]^2$ vs. log $[\mathrm{Y}']$ should be two (within the approximation that changes in the activity coefficients are negligible). The results for extractions in which the HDPM to uranium ratio was large and in which the $[\mathrm{NO}_3^-]$ remains essentially constant (curve A in Fig. 2) did fall on a straight line of slope two when log D_{U} was plotted vs. log [HDPM′]. A similar plot for extractions in which uranium was always in excess and in which the $[\mathrm{NO}_3^-]$ varied appreciably (curve *B* in Fig. 2) fell on a straight line of slope one when log $D_{\mathrm{U}}/[\mathrm{NO}_3^-]^2$ was plotted vs. log [HDPM′]. This suggests the formation of a 1:1 complex. The formation constant of the 1:1 complex, K_1', was calculated from the data for curve *B*, Fig. 2 and found to be $1.58 \pm 0.10 \times 10^3$.

The value of K_2' (0.01 M) for the extractions from 0.01 M nitric acid was 2.08×10^8 (Table 2). The results for a series of extractions from 1 M nitric acid are also given in Table 2. A 2:1 combining ratio is assumed for both HDPM and TOPO and K_2' (1 M) values are calculated. The average value for K_2' (1 M) of 1.05×10^6 for HDPM is nearly what is expected if the variation in α is taken into consideration. Taking α as 0.062 and 1 for the cases of 1 M and 0.01 M acid, respectively, one obtains from $[K_2'\ (1\ \mathrm{M})]/[(0.062)^2]$, a calculated value for K_2' (0.01 M) of 2.78×10^8. This is in agreement with the experimental value obtained for K_2' (0.01 M) considering that changes in the activity coefficients have been neglected.

The value of α for TOPO (0.089) in 1 M nitric acid gives a calculated value of 1.15×10^7 for K_2' (TOPO) for solutions of low acid concentration where $\alpha = 1$. It is seen that the over-all equilibrium constant for the extraction of uranium (VI) from nitric acid media with HDPM is approximately twenty times as great for TOPO

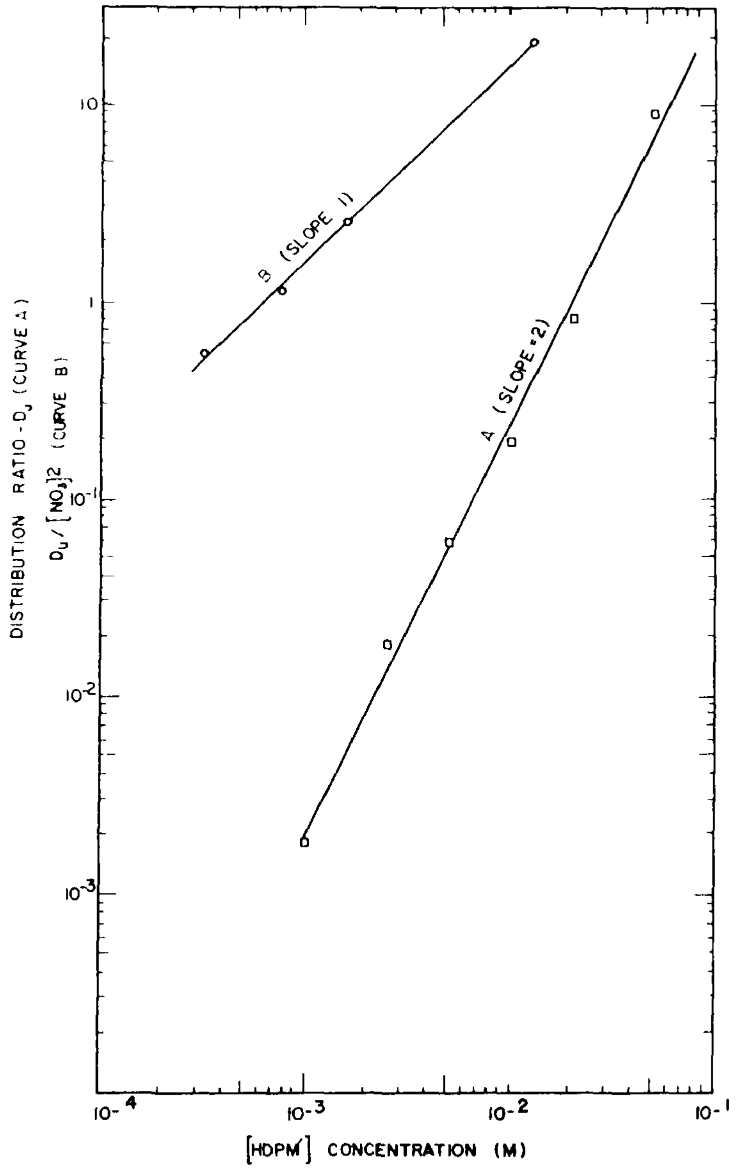


FIG. 2 — Extraction of uranium (VI) as function of HDPM concentration

Curve *A* $[UO_2^{2+}]_i$ $(5.16 \times 10^{-5}$ M$)$,
$[HNO_3]_i$ $(2.48 \times 10^{-3}$ M$)$

Curve *B* $[UO_2^{2+}]$ $(0.1$ M$)$,
$[HNO_3]_i$ $(6.8 \times 10^{-3}$ M$)$

Diluent — 1,2-dichlorobenzene Phase ratio — 1 Temperature 25° ± 2°C, 10 min equilibration time for both curves

Effect of mineral acids at various concentrations on the extraction of uranium (VI)

The variation in the distribution ratio of uranium (IV) into HDPM as a function of the acid concentration of the aqueous phase is shown in Fig. 3. For comparison purposes, the data obtained by WHITE and ROSS[3] on TOPO are also shown. It should be noted that the initial concentration of HDPM was 0.05 M while that of TOPO was 0.1 M. Furthermore, the mole ratio of organophosphorus compound to uranium was 3:1 in the case of HDPM but 26.5:1 in the case of TOPO. Consequently, the equilibrium concentration of uncomplexed extractant is much lower in the case of HDPM.

TABLE 2.—K_2' VALUES FOR THE EXTRACTION OF URANIUM (VI) WITH HDPM AND TOPO FROM NITRIC ACID

$[HDPM]_i$*	$[UO_2^{2+}]_i$ ($\times 10^3$)	D_1	K_2' (1 M) ($\times 10^{-6}$)	K_2' (0.01 M) ($\times 10^{-8}$)	$[TOPO]_i$	$[UO_2^{2+}]_i$	D_1	K_2' (1 M) ($\times$ 10 [illegible])
0.1	25.0	2860	1.14		0.1	0.025	199	0.79
0.0667	16.7	1060	0.95		0.04	0.01	35.4	0.84
0.0445	11.1	414	0.83		0.1	0.0167	416	0.94
0.0320	8.0	213	0.83		0.06	0.01	147	0.91
0.06	10.0	2350	1.47		0.1	0.0125	495	0.85
0.024	4.0	265	1.03		0.064	0.008	213	0.93
0.012	2.0	58.8	0.92		0.016	0.004	7.89	1.00
0.0024	0.4	3.82	1.22		0.008	0.002	2.55	0.96
0.05	0.0513	52.13		2.09	0.024	0.004	25.1	0.95
0.05	0.132	60.51		2.45	0.012	0.002	6.62	0.91
0.05	0.263	51.10		2.08	0.032	0.004	54.6	0.94
0.05	0.395	47.94		1.98	0.016	0.002	14.4	0.90
0.05	0.524	43.55		1.81				
Average values			1.05	2.08				0.91

* Subscript *i* denotes initial concentration.

The variations in distribution ratio of uranium into HDPM or TOPO from nitric, hydrochloric, suphuric and phosphoric acid are similar as seen in Fig. 3. The results for phosphoric acid are not shown but were very low for HDPM, D_{U} values less than 10^{-3}, and were also reported to be low for TOPO.[3] The difference in extraction of uranium from perchloric acid media by TOPO and HDPM is surprisingly great. It should be noted that WHITE and ROSS[3] used cyclohexane as the diluent for TOPO. Work in this Laboratory, however, has shown that similar results are obtained with TOPO when 1,2-dichlorobenzene is used as the diluent rather than cyclohexane.

In conclusion, HDPM is rather similar to TOPO as an extractant for uranium (VI) from mineral acid solutions except for perchloric acid. The distribution ratio of uranium (VI) is generally larger for HDPM than for TOPO and in the case of extraction from perchloric acid media it is several orders of magnitude larger. The relatively

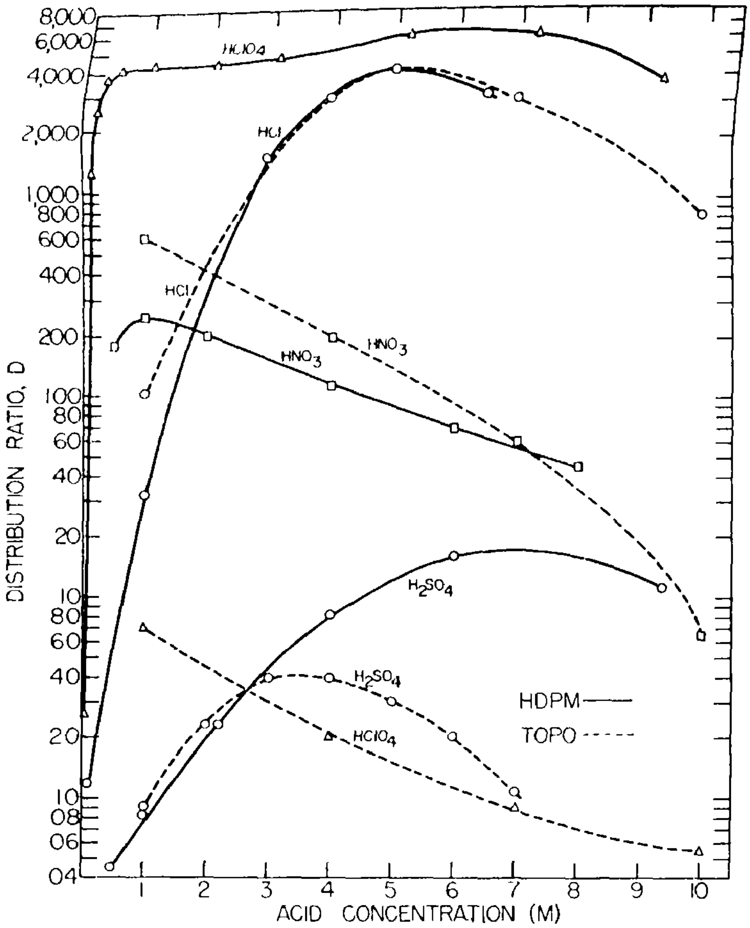


FIG. 3. Extraction of uranium (VI) with HDPM and TOPO as a function of acid concentration

Data on TOPO (dotted lines) from WHITE and ROSS[3]. HDPM, 0.05 M solution in 1,2-dichlorobenzene. Phase ratio = 1. Ratio HDPM to uranium (VI) = 3. Extraction time = 10 min

large values for the distribution of uranium (VI) from perchloric media into HDPM are not unique with uranium It has been found that many other metal perchlorates extract very well into 1,2-dichlorobenzene containing HDPM The latter work will be described in future publications

Acknowledgements—The authors wish to acknowledge the contributions of Mr J J RICHARD, who prepared the HDPM used in this investigation, Mr K E BURKE, who initiated work on the use of HDPM as a solvent extractant, and Messrs J W FERGUSON and J BIRK, who assisted with some of the experimental work

J Inorg Nucl Chem, 1963, Vol 25 pp 963 to 970 Pergamon Press Ltd Printed in Northern Ireland

THE CO-ORDINATION CHEMISTRY OF MOLYBDENUM—I

SOME COMPLEXES OF MOLYBDENUM(V) WITH 2 2'-DIPYRIDYL

P C H MITCHELL
Department of Chemistry, The University, Nottingham

(*Received* 14 *December* 1962)

Abstract -The preparations and chemical magnetic and spectroscopic properties of the following complexes of molybdenum(V) with 2 2'-dipyridyl are described $MoO_2Cldipy$ (I), $Mo_2O_3Cl_4(dipy)_2$ (II), and $MoOCl_3dipy$(III) According to the magnetic moments I and II are polymerized and III is a monomer Possible structures of the complexes are discussed

IN a previous paper(1) the preparation and properties of a complex of molybdenum(V) with 1 10-phenanthroline were described During the earlier work the formation of dark precipitates was observed when ethanolic solutions of ammonium oxopentachloromolybdate(V), $(NH_4)_2MoOCl_5$, and 2 2'-dipyridyl were mixed These precipitates have now been shown to contain complexes of molybdenum(V) with dipyridyl and the present paper describes their preparations and properties These compounds are of interest as further examples of complexes of dipyridyl with a metal in a high oxidation state and may be compared with the dipyridyl complexes of vanadium(IV) and iron(III) (2)

EXPERIMENTAL

Materials

The following compounds were obtained commercially or prepared by standard methods molybdenum pentachloride (Found Mo, 35 11, Cl, 64 20 Calc for $MoCl_5$ Mo 35 10, Cl, 64 90%), molybdenyl hydroxide(3) (Found, Mo, 58 7 Calcd for $MoO(OH)_3$ Mo 58 9%) ammonium oxopentachloromolybdate(V)(4) (Found Mo, 29 7 Calcd for $(NH_4)_2MoOCl_5$ Mo, 29 5%), 2 2'-dipyridyl(5) (m p 70 5°, lit 70 5–71 5°)

Commercial absolute ethanol was purified(6) and carbon tetrachloride was refluxed with potassium hydroxide pellets and distilled before use

Analyses

Molybdenum was determined gravimetrically as molybdyl oxinate after decomposing the complexes by heating to fuming with a 1 1 mixture of concentrated nitric and sulphuric acids chloride gravimetrically as silver chloride after decomposing the complexes with dilute nitric acid dipyridyl spectrophotometrically by extraction with chloroform of the solution obtained by refluxing the complexes with 0 2N sodium hydroxide The molybdenum oxidation number was determined by oxidation of the complexes with ceric sulphate

Preparations

All reactions were carried out under dry nitrogen, excess dipyridyl being used to ensure completion

Oxo-μ-dioxochloro(2 *2'-dipyridyl*)*molybdenum*(V), $Mo_2O_4Cl_2dipy_2$, (I) A filtered, deep brown solution of ammonium oxopentachloromolybdate(V) (1.6 g) in ethanol (100 ml) was added dropwise to a refluxing solution of dipyridyl (1.5 g) in ethanol (100 ml). There was an immediate dark precipitate. The suspension was allowed to cool and filtered by suction. The precipitate was washed with ethanol and petroleum ether and dried in vacuo over KOH pellets. The product (1.5 g) was a dark red brown powder. (*Found*: Mo, 29.73, Cl, 11.05, dipy, 49.04. $(C_{10}H_8N_2)ClMoO_2$ requires Mo, 30.03, Cl, 11.10, dipy, 48.86%. The oxidation number of the molybdenum was 5.0.)

---

(1) P C H MITCHELL and R J P WILLIAMS, *J Chem Soc*, 4570 (1962)
(2) W W BRANDT, F P DWYER and E C GYARFAS, *Chem Rev* **54**, 959 (1954)
(3) W G PALMER, *Experimental Inorganic Chemistry*, p 406 Cambridge (1959)
(4) J P SIMON and P SOUCHAY, *Bull Soc Chim France*, 1402 (1956)
(5) G M BADGER and W H F SASSE *J Chem Soc* 616 (1956)
(6) P A LEIGHTON, R W CRARY, L T SCHIPP, *J Amer Chem Soc* **53**, 3017 (1931)

Oxo-μ-oxodichloro(2,2'-dipyridyl)molybdenum(V), $Mo_2O_3Cl_4(dipy)_2$, (II). Ethanol (10 ml) was added dropwise to a flask containing molybdenum pentachloride (1.5 g) and the mixture was stirred. Hydrogen chloride was evolved and the resulting molybdenum(V) solution was deep green. To this solution was added dropwise and with stirring a solution of dipyridyl (1.5 g) in ethanol (25 ml). There was an immediate dark precipitate. The suspension was centrifuged and the precipitate was washed with ethanol and petroleum ether and dried *in vacuo* over KOH pellets. The product (2.0 g) was a red brown powder. (*Found*: *Mo*, *27.56*, *Cl*, *20.47*, *dipy*, *44.72*. $(C_{10}H_8N_2)_2Mo_2O_3Cl_4$ *requires Mo*, *27.65*, *Cl*, *20.45*, *dipy*, *44.99%*. *The oxidation number of the molybdenum was 5.0.*)

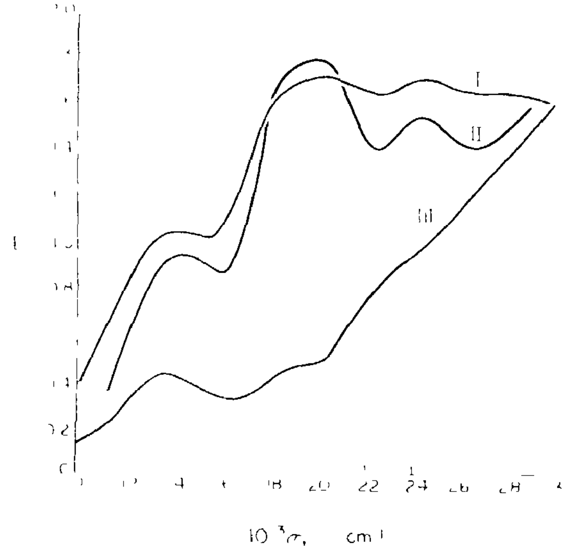


FIG. 1. – The reflexion spectra (optical density against frequency) of $MoO_2Cldipy$ (I), $Mo_2O_3Cl_4$ $(dipy)_2$ (II) and $MoOCl_3dipy$ (III).

Oxotrichloro(2,2'-dipyridyl)molybdenum(V), $MoOCl_3dipy$(III). This compound was obtained when molybdenum pentachloride and dipyridyl were heated in solution in carbon tetrachloride containing a trace of moisture. A solution of dipyridyl (2.5 g) in carbon tetrachloride (100 ml) was added dropwise to a solution of molybdenum pentachloride (1.4 g) in carbon tetrachloride (100 ml). At first there was a slight red precipitate but as more dipyridyl was added the colour of the solution was rapidly discharged and a pale yellow-green precipitate formed. The suspension was refluxed overnight and filtered by suction. The filtrate was washed with carbon tetrachloride and petroleum ether and dried in vacuo over KOH pellets. The product (1.3 g) was a pale khaki solid. (Found: Mo, 26.21, Cl, 27.70, dipy, 40.94. Calcd. for $C_{10}H_8N_2Cl_3MoO$: Mo, 25.62, Cl, 28.42, dipy, 41.69%. The oxidation number of the molybdenum was 5.0.)

Some properties of the complexes

The complexes were insoluble in water and dilute acids but gave yellow suspensions on warming. Dipyridyl was extracted by chloroform from the aqueous suspensions showing that hydrolysis had occurred. The complexes were slowly oxidized (with loss of colour) when the suspensions in dilute nitric acid were warmed.

All three compounds dissolved in aqueous sodium hydroxide solution giving deep purple solutions which rapidly decolourized and deposited black precipitates.

---

(7) H. B. GRAY and C. R. HARE, *Inorg. Chem.* **1**, 363, 831 (1962).

I and II were only very slightly soluble in common organic solvents (nitromethane, nitrobenzene pyridine, methyl cyanide, dimethyl sulphoxide) giving red solutions which rapidly lost their colour even under nitrogen III was more soluble in these solvents giving yellow solutions the colours of which quickly faded The relative insolubility of I and II is consistent with their formulation as dimers or polymers (see below)

Magnetic susceptibilities

The Gouy method was used to measure the susceptibilities of the complexes at room temperature A magnetic field of ca 6,000 G was provided by a permanent magnet and the Gouy tubes were calibrated for measurements on the finely powdered solids with cobalt mercury thiocyanate with an assumed gramme susceptibility of 16 44 10^{-6} cgs at 20°(8) At least two determinations were made on different samples of each complex Apparent magnetic moments were calculated using the formula μ_{eff} $2.839(\chi'_M T)^{\frac{1}{2}}$ (where χ'_M is the susceptibility corrected for diamagnetism)(9)

Ultra-violet and visible spectra

A Unicam SP 500 spectrophotometer was used Since the complexes were insoluble or gave unstable solutions in the solvents available the reflexion spectra of the solids were measured against a magnesium carbonate standard

Infra-red spectra

A Unicam SP 100 spectrophotometer was used to record the spectra of the solids in the range 700 3500 cm^{-1}

RESULTS

Preparation of the complexes

Precipitates of the complex MoO_2Cldipy were obtained during attempts to study spectrophotometrically the reaction between ethanolic solutions of molybdenum(V) and dipyridyl In general, the monochloro complex was obtained from brown dilute ethanolic solutions of ammonium oxopentachloromolybdate(V) whereas the dichloro-complex $Mo_2O_3Cl_4(dipy)_2$ was obtained from the more concentrated green solutions of molybdenum pentachloride in ethanol The trichloro-complex could be obtained only from solutions of molybdenum pentachloride in carbon tetrachloride containing a trace of moisture (i e under conditions when the hydrolysis of molybdenum(V) was minimized)

Magnetic moments

The magnetic moments of the complexes are given in Table 1 The value for $MoOCl_3$dipy was close to the spin only moment for molybdenum(V) but the other two complexes had much lower moments probably because of polymerization (see below)

TABLE 1 —MAGNETIC PROPERTIES OF THE COMPLEXES

Complex	$10^6\chi_M$	$10^6\chi_D$	$10^6\chi'_M$	T (K)	$\mu(\beta)$
MoO_2Cldipy	−75	167	92	298	0 47
$Mo_2O_3Cl_4(dipy)_2$	107	187	294	299	0 84
$MoOCl_3$dipy	1281	207	1488	293	1 87

(χ_M – molar susceptibility per molybdenum, χ_D = diamagnetic correction Estimated uncertainty in μ = ±0 15 β)

---

(8) B N FIGGIS and R S NYHOLM, *J Chem Soc* 4190 (1958)

(9) B N FIGGIS and J LEWIS, in *Modern Co-ordination Chemistry* p 403, Interscience New York, (1960)

Infra-red spectra

Details of the infra-red spectra of the complexes are given in Table 2 and probable assignments of the main bands in Table 3. The interpretation of the spectra is complicated by the presence of the dipyridyl bands. The infra-red spectra of dipyridyl and of its cation and of molybdenyl hydroxide are given for comparison.

(a) *Metal-oxygen stretching frequencies.* A value of 967 cm^{-1} has been assigned for the Mo(V)=O stretching frequency in K_2MoOCl_5 and a strong band in this region is expected for all compounds containing a metal-oxygen double bond.(10) Molybdenyl hydroxide (almost certainly a polymer) has three bands in the region 700–1000 cm^{-1}. The very strong band at 977 cm^{-1} may be assigned to the asymmetric Mo—O

TABLE 2. INFRA-RED SPECTRA

Compound	Infra-red bands
2,2'-dipyridyl*	713*sh,m* 742*sh,m* 760*vs* 893*m* 981*sh,m* 996*s* 1042*s* 1069*m* 1093*s* 1150*m* 1175*m* 1218*w* 1258*m* 1271*w* 1320*w,b* 1425*vs* 1568*m* 1590*vs* 1620*sh,w* 1671*w* 1719*w* 1811*w* 1901*w* 1985*w* 2195*w* 2299*w* 2733*m*
dipyH$_2^{2+}$ †	713*s* 763*sh,s* 771*s* 892*m* 968*s* 1031*s* 1080*m* 1099*w* 1160*sh,m* 1175*m* 1232*m* 1243*m* 1283*s* 1315*sh,m* 1324*sh,m* 1370*sh,m* 1510*sh,m* 1540*sh,m* 1560*sh,m* 1570*sh,m* 1576*sh,m* 1600*s* 1610*sh,m* 1620*sh,m* 1648*sh,m* 1912*w* 1973*w* 2045*w* 2340*m* 2628*w* 2673*w* 2729*w*
MoO_2Cldipy	721*m* 742*s* 775*s* 812*w* 848*sh,w* 901*m* 920*sh,m* 941*sh,s* 952*vs* 1020*w* 1030*m* 1046*w* 1065*w* 1077*w* 1107*m* 1122*w* 1158*m* 1174*m* 1230*m* 1250*m* 1273*sh,m* 1321*s* 1499*m* 1568*m* 1577*m* 1601*s* 1609*sh,m* 2674*w* 2729*w*
$Mo_2O_3Cl_4$(dipy)$_2$	720*sh,m* 741*sh,m* 774*s* 798*m* 849*w* 904*s* 936*s* 966*vs* 1020*w* 1029*m* 1046*w* 1062*w* 1075*w* 1109*m* 1125*w* 1158*m* 1174*m* 1227*m* 1248*m* 1284*m* 1316*s* 1499*m* 1566*w* 1575*w* 1602*s* 1610*m* 2671*w* 2729*w*
$MoOCl_3$dipy	720*sh,m* 745*m* 773*s* 805*w* 849*w* 912*vs* 940*m* 979*vs* 1020*m* 1032*s* 1047*w* 1068*m* 1077*m* 1110*m* 1124*m* 1165*m* 1180*m* 1223*m* 1250*s* 1290*sh,m* 1321*s* 1500*m* 1568*m* 1575*w* 1603*s* 1610*m* 2680*m* 2729*m*
$MoO(OH)_3$	714*s,b* 757*s,b* 895*s* 977*vs* 1162*w* 1215*w* 1619*m* 3205*s,b* 3413*s,b*

* Zone refined dipyridyl kindly supplied by Imperial Chemical Industries Limited.

† Obtained by recrystallizing dipyridyl from concentrated hydrochloric acid.

TABLE 3.—PROBABLE ASSIGNMENTS OF THE MAIN INFRA-RED BANDS

Dipy	DipyH$_2^{2+}$	MoO_2Cldipy	$Mo_2O_3Cl_4$dipy$_2$	$MoOCl_3$dipy	$MoO(OH)_3$	Assignment
		952*vs*	966*vs*	979*vs*	977*vs*	Mo=O str
					895*s*	Mo—O str?
					757*s,b*	Mo—O chain
					714*s,b*	vibrations
	2340*m,b*					$\geq N^+$—H str
1590*s*	1600*s*	1601*s*	1602*s*	1603*s*		
	1610*m,sh*	1609*m,sh*	1610*m*	1610*m*		
1425*vs*						dipyridyl
1320*w,b*	1315*m,sh*	1321*s*	1316*s*	1321*s*		bands
	771*s*	775*s*	774*s*	773*s*		
760*vs*	763*s,sh*					

(*b* = broad, *m* = medium, *s* = strong, *sh* = shoulder, str = stretch, *vs* = very strong, *w* = weak.)

---

(10) C. G. BARRACLOUGH, J. LEWIS and R. S. NYHOLM, *J. Chem. Soc.* 3552 (1959); H.-L. KRAUSS and W. HUBER, *Ber. Dtsch. Chem. Ges.* **94**, 2864 (1961).

stretch, that at 895 cm^{-1} possibly to a symmetric Mo—O stretch, the broader and weaker bands at 757 and 714 cm^{-1} to vibrations of the metal-oxygen chain (—Mo—O—Mo—O— cf. reference 10). For each of the dipyridyl complexes only one band can be assigned with any certainty to the Mo=O stretch (see Table 3) since the weaker bands in the region 900–1000 cm^{-1} could arise from co-ordinated dipyridyl

(b) Possible O—H frequencies The broad bands with frequencies greater than 3000 cm^{-1} in molybdenyl hydroxide are due to O—H stretching vibrations There are no peaks in this region in the dipyridyl complexes Thus formulation of complex II (and the corresponding phenanthroline complex(11)) with hydroxide (i e as MoO(OH) Cl_2dipy) appears to be incorrect (The analytical figures for this formulation and for $Mo_2O_3Cl_4(dipy)_2$ are only slightly different)

(c) Dipyridyl frequencies The infra-red spectra of dipyridyl and its cation are given in Table 3 and are in good agreement with earlier measurements (11) In the complexes the dipyridyl bands are shifted to higher frequencies compared with the free ligand indicating that the dipyridyl is co-ordinated to the metal The infra-red spectra also show that the dipyridyl is not protonated, for example, there are no "immonium" ($\rangle N^{+}$—H) bands (12)

Ultra-violet and visible spectra of the complexes

Since the complexes were insoluble or decomposed in the solvents tried, reflexion spectra of the powdered solids were measured in the range 340–1000 mμ The positions of the absorption maxima are given in Table 4 and the spectra are shown in the figure The spectra of complexes I and II are similar in appearance and the extinction coefficients are about the same, but the spectrum of complex III is quite different, having a long tail into the visible and two weak peaks

TABLE 4 ELECTRONIC SPECTRA OF THE COMPLEXES

Compound	λ_{max}	$10^{-3}\sigma_{max}$	Intensity	Probable transition
MoO_2Cldipy*	720	13 9	Medium	$^2B_2 \rightarrow {}^2E(I)$
	495	20 2	Strong	dipy →Mo, charge transfer
	410	24 4	Strong	$^2B_2 \rightarrow {}^2B_1$?
$Mo_2O_3Cl_4dipy_2$†	704	14 2	Medium	$^2B_2 \rightarrow {}^2E(I)$
	513	19 5	Strong	dipy→Mo, charge transfer
	413	24 2	Strong	$^2B_2 \rightarrow {}^2B_1$?
$MoOCl_3$dipy	735	13 6	Weak	$^2B_2 \rightarrow {}^2E(I)$
	532	18 8	Weak	$^2B_2 \rightarrow {}^2B_1$
	(435)†	23 0	Medium	dipy →Mo charge transfer

λ_{max} is the wavelength of maximum absorption in millimicrons and σ_{max} is the frequency of maximum absorption in cm^{-1} Data in parentheses are for shoulders The probable transitions are discussed in the text, see also Reference(7)

DISCUSSION

There has been very little previous work on complexes of molybdenum(V) with dipyridyl An insoluble oxalato complex, K[$MoO_2(C_2O_4)$dipy], has been obtained by mixing solutions of K[$MoO_2(C_2O_4)$] and dipyridyl(13) and dipyridyl complexes are thought to be present in the deep reddish purple solutions formed in the reduction of molybdate by chlorostannous acid in the presence of dipyridyl (14) A few complexes of molybdenum(V) with other nitrogen heterocyclic ligands have been described, for example, MoOCl$_3$pyr (pyr = pyridine)(15) and MoOCl$_3$phen (16) They were described as red brown insoluble solids, but Wardlaw(17) was unable to repeat the preparation of the pyridine complex The reaction between molybdenum pentachloride and pyridine in a sealed tube involves reduction of the molybdenum(V), the products being pyridine adducts of molybdenum tetrachloride (18) There is as yet no evidence for a similar reaction with dipyridyl although the latter would be expected to stabilize lower oxidation states more strongly than pyridine However, the complexes described in this paper were prepared under conditions leading to the formation of molybdenum(V) oxycations and oxide is known to stabilize molybdenum(V) relative to the lower oxidation states The reaction between molybdenum(V) and dipyridyl under rigorously anhydrous conditions is being investigated

---

(11) A A SCHILT and R C TAYLOR, *J Inorg Nucl Chem*, **9**, 211, (1959), B MARTIN W R MCWHINNIE and G M WAIND, *J Inorg Nucl Chem* **23**, 207 (1961)

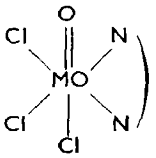
(12) A R KATRITZKY, *Quart Rev* **13**, 353 (1959)

(13) G A BARBIERI and A MALAGUTI, *Mem Accad Sci Ist Bologna* **9**, 3, (1951) [Chem Abst **47**, 8574d (1953)]

The empirical formulae of the complexes are based on analyses for molybdenum, chloride and dipyridyl and determinations of the molybdenum oxidation number It was not possible to determine oxide directly and oxide is included in the empirical formulae to give overall charge neutrality for molybdenum(V) consistent with the analyses For each complex agreement between the observed and calculated analyses is good and the presence of molybdenum(V) oxycations is confirmed by the infra-red spectra of the complexes

Because of the insolubility of the complexes molecular weight determinations were not possible, but it is fairly certain that the complexes I and II, with low magnetic moments, are polymerized and that III, with a normal moment, is a monomer (1 19)

The monomeric complex III is one of a series of complexes of the general formula MoOCl$_3$L$_2$ (e g L = Ph$_3$PO, Ph$_3$AsO, Me$_2$SO (20)) and its structure is almost certainly as shown below



Its formation may be written as follows

$$\mathrm{MoCl_5} \xrightarrow[\text{or EtOH}]{\mathrm{H_2O}} \mathrm{MoOCl_3} \xrightarrow{\text{dipy}} \mathrm{MoOCl_3dipy}$$

Formation of the complexes I and II illustrates the strong tendency of molybdenum(V) to form polymeric oxychloride cations Since the ethanol used as a solvent was not exhaustively dried it is likely that the solutions of $(NH_4)_2MoOCl_5$ contain hydrolysed and polymerized species * The constitution of molybdenum(V) solutions

---

* The spectra of solutions of $(NH_4)_2MoOCl_5$ in ethanol have absorption maxima at 310, 450 and 720 mμ Beer's law is not obeyed and the deviations indicate polymerization of the molybdenum(V) species (unpublished observations of the author) It is likely that ethanolysis is the initial reaction in the formation of MoOCl$_3$ from MoCl$_5$ (20)

(14) A S Komarovskii and N S Poluektov, *J Applied Chem* (U S S R) **10**, 565 (1937)

(15) G Scagliarini, *Atti R Accad Lincei* vi, **1**, 676 (1925)

(16) G Spengler and J Gansheimer, *Angew Chem* **69**, 523 (1957)

(17) R G James and W Wardlaw, *J Chem Soc* 2145 (1927)

(18) W Wardlaw and H W. Webb, *J Chem Soc* 2100 (1930)

(19) C M French and J H Garside, *J Chem Soc* 2006 (1962)

(20) S M Horner and S Y Tyree, *Inorg Chem* **1**, 122 (1962)

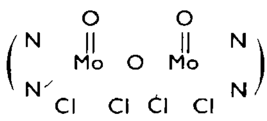
in hydrochloric acid has been discussed by SIMON and SOUCHAY⁽⁴⁾ and more recently by GRAY and HART⁽⁷⁾ and by HAIGHT⁽²¹⁾ The initial paramagnetic hydrolysis product of $MoOCl_5^{2-}$ has been formulated as $Mo_2O_3Cl_2^{2+}$⁽⁴⁾ and $Mo_2O_3Cl_8^{4-}$⁽²¹⁾, further hydrolysis gives diamagnetic dimers The formulation of the polymeric dipyridyl complexes is in accordance with this hydrolysis scheme Thus the complex $Mo_2O_3Cl_4dipy_2$ is obtained under conditions which would be expected to produce less hydrolysis than the conditions under which the complex $MoO_2Cldipy$ is obtained and the former complex has a higher magnetic moment than the latter The respective reactions may be written as follows

$$MoCl_5 \xrightarrow[\text{or EtOH}]{H_2O} MoOCl_3 \xrightarrow[\text{in ethanol}]{H_2O} Mo_2O_3Cl_4 \xrightarrow{\text{dipy}} Mo_2O_3Cl_4(dipy)_2$$

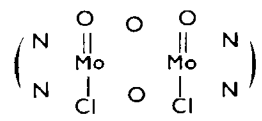
$$(NH_4)_2MoOCl_5 \xrightarrow[\text{ethanol}]{\text{in}} NH_4Cl + MoOCl_3 \xrightarrow{H_2O} Mo_2O_3Cl_4$$

$$\xrightarrow{H_2O} Mo_2O_4Cl_2 \xrightarrow{\text{dipy}} Mo_2O_4Cl_2(dipy)_2$$

The empirical formula units MoO_2Cl and $Mo_2O_3Cl_2$ occur in other molybdenum(V) complexes, for example, with aniline⁽¹⁶⁾ and in the thiocyanate complexes $R_4Mo_2O_3(NCS)_8$ and $(pyH)_4Mo_2O_3(NCS)_6SO_4$ ⁽²²⁾ It is suggested that the Mo_2O_3 unit contains a single oxide bridge and the MoO_2 unit a double oxide bridge so that the dipyridyl complexes are written



II



I

In view of the work of LEWIS *et al*⁽²³⁾ on the magnetic properties of polymeric complexes it may seem surprising that the complex with the higher magnetic moment (II) should be formulated with a single oxide bridge, but it should be noted that there should be a greater possibility of direct metal metal bonding in I than in II ⁽¹⁾

Even with a large excess of dipyridyl it was not possible to obtain complexes in which the dipyridyl/molybdenum ratio exceeded one although molybdenum(V) does form 1 2 complexes with oxine ⁽¹⁾

The peaks in the visible spectra of the dipyridyl complexes may be discussed with reference to the spectra of $(NH_4)_2MoOCl_5$⁽⁷⁾ and other organic complexes of molybdenum(V) ⁽¹⁾ It is certain that the broad weak peaks near 14 000 cm⁻¹ in the spectra of the dipyridyl complexes are due to the first crystal field transition $^2B_2 \rightarrow {}^2E(I)$ The second crystal field transition ($^2B_2 \rightarrow {}^2B_1$) of the oxychloride complexes occurs at 22,600 cm⁻¹ Its intensity in $(NH_4)_2MoOCl_5$ is the same as that of the first transition, but is much greater in the polymeric complexes Similarly the ratio of the intensities of the second and first peaks for the polymeric dipyridyl complexes (I and II) is much greater than for the monomeric complex (III) (cf the figure) Many complexes of molybdenum(V) with organic ligands have a strong metal to ligand charge transfer transition in the region 17,000–20,000 cm⁻¹ ⁽¹⁾ It is therefore suggested that the peaks

---

⁽²¹⁾ G P HAIGHT, *J Inorg Nucl Chem* **24**, 663 (1962)

⁽²²⁾ R G JAMES and W WARDLAW, *J Chem Soc* 2726 (1928)

⁽²³⁾ A EARNSHAW and J LEWIS, *J Chem Soc* 396 (1961) at 20,000 cm^{-1} in the polymeric dipyridyl complexes arise from the charge transfer transition and that the peaks at 24,000 cm^{-1} are due to the $^2B_2 \rightarrow {}^2B_1$ transition In the complex $\mathrm{MoOCl_3dipy}$, however, it appears that the relatively weak peak at 18,800 cm^{-1} is the second crystal field transition and that the ligand to metal charge transfer transition is displaced to higher freqencies compared with the polymeric complexes

It is not yet possible to say much about the bonding between the molybdenum and the dipyridyl, it is likely that in complexes with metals in high oxidation states dipyridyl behaves as a π-donor as well as a σ-donor ligand It is worth noting that molybdenum resembles other transition metals in the ability of the oxycations of the higher oxidation states to coordinate with dipyridyl and phenanthroline For example iron(III) as well as forming tris-dipyridyl and phenanthroline complexes also forms a dimeric oxychloride complex $\mathrm{phen_4Fe_2(OH)_2Cl_4}$ and vanadium(IV) forms similar complexes derived from $\mathrm{VO^{2+}}$ (2)

Acknowledgements This work was carried out during the tenure of an Imperial Chemical Industries Limited Research Fellowship at the University of Nottingham

J Inorg Nucl Chem, 1963 Vol 25 pp 971 to 974 Pergamon Press Ltd Printed in Northern Ireland

SOME ALKYL ISOCYANIDE COMPLEXES OF IRON

S C MALHOTRA
Explosives Department, Experimental Station, E I du Pont
de Nemours and Co , Wilmington, Delaware

(*Received* 18 *February* 1963)

Abstract—Novel cyanopentakis(methyl isocyanide)iron (II) iodide was synthesized by the controlled alkylation of the known dicyanotetrakis(methyl isocyanide)iron (II) with methyl iodide Reaction of potassium ferrocyanide with methyl bromide gave hexakis(methyl isocyanide)iron (II) bromide, which yielded the dicyanotetrakis(methyl isocyanide)iron (II) upon thermal decomposition These complexes were transformed into the benzyl analogues by reaction with benzyl bromide The products characterized were the known cyanopentakis(benzyl isocyanide)iron (II) bromide and dicyanotetrakis(benzyl isocyanide)iron (II)

SEVERAL hexa- and tetra-alkyl isocyanide complexes of iron (II) of the general formulae $(RNC)_6FeX_2$ and $(RNC)_4Fe(CN)_2$ respectively have been mentioned in the literature (1–13) Malatesta has reviewed many other complexes of the above type (14)

We have successfully synthesized for the first time a hitherto unknown and novel penta-alkyl isocyanide complex of iron, $(CH_3NC)_5Fe(CN)I\ H_2O$ and have discovered an alternate route for the preparation of another novel pentabenzyl isocyanide complex of iron, $(C_6H_5CH_2NC)_5Fe(CN)Br\ H_2O$, which was only recently reported by HELDT (9–13)

EXPERIMENTAL

All materials employed in this work were reagent grade chemicals and were used without further purification Anhydrous potassium ferrocyanide was prepared by heating the potassium ferrocyanide trihydrate (General Chemical Division, Allied Chemical and Dye Corp New York N Y) at 150° under reduced pressure (24 mm) for 4 hr (8)

Halogens were determined by precipitation of the silver halides from dilute nitric acid solutions Iron was determined volumetrically by titration with potassium permanganate after decomposition of the samples with nitric acid and reduction in a Jones Reductor

Melting points are uncorrected Infra-red spectra were recorded with Perkin Elmer Infracord Spectrophotometer

---

(1) E G J HARTLEY, *Proc Chem Soc* **26,** 90 (1910)

(2) E G J HARTLEY, *J Chem Soc* **97,** 1066 (1910)

(3) E G J HARTLEY, *J Chem Soc* **97,** 1725 (1910)

(4) E G J HARTLEY, *Proc Chem Soc* **29,** 188 (1913)

(5) E G J HARTLEY, *J Chem Soc* **103,** 1196 (1913)

(6) J W SMITH, *Science Progress*, **36,** 656 (1948)

(7) H M POWELL, *Proceeding Symposium on Co-ordination Chem Copenhagen* 36 (1953) (*Chem Abstr* **49,** 15593 (1955))

(8) W Z HELDT, *J Org Chem* **26,** 3226 (1961)

(9) W Z HELDT, *J Inorg Nucl Chem* **22,** 305 (1961)

(10) W Z HELDT, *J Inorg Nucl Chem* **24,** 73 (1962)

(11) W Z HELDT, *J Inorg Nucl Chem* **24,** 265 (1962)

(12) W Z HELDT, *J Org Chem* **27,** 2604 (1962)

(13) W Z HELDT, *J Org Chem* **27,** 2608 (1962)

(14) L MALATESTA, *Progress in Inorganic Chemistry* (Edited by F A COTTON) Vol 1, p 320 Interscience, New York (1959)

Synthesis of hexakis(methyl isocyanide)iron (II) bromide

A mixture containing potassium ferrocyanide (37 g, 100 mmole) methyl bromide (100 g, 1053 mmole) and acetonitrile (100 ml), was heated in a closed 320 ml stainless steel autoclave at 100° for 6 8 hr under autogenous pressure The mass was extracted with additional acetonitrile (100 ml) and the solution was separated from the insoluble material The product in the solution was purified by repeated crystallizations from hot acetonitrile m p 196–98° It was soluble in water, ethanol and acetonitrile Found C 29 49, H 4 96 N, 16 99, Fe, 11 54 Calc for $(CH_3NC)_6FeBr_2\ 2H_2O$ C 28 93 H 4 42, N 16 87, Fe, 11 21 % Infra-red spectrum (KBr μ) 2 9(s), 3 32 (w), 3 39 (w), 3 95 (w), 4 47 (s), 5 35 (w), 6 13 (m), 6 93 (m) 7 1 (*m*) and 9 0 (w)

Synthesis of dicyanotetrakis(methyl isocyanide)iron (II)

A sample of hexakis(methyl isocyanide)iron (II) bromide (6 9 g) was heated at 140° for 8 hr at 10^{-1} mm in a 25 mm Pyrex tube that was closed at one end, whereupon methyl bromide was liberated and was collected in a dry ice acetone trap The residual solid (3 3 g) was purified by crystallization from hot chloroform The product decomposed without melting at 255–57° Yield = 88 per cent Found C, 43 62, H 4 70 N, 30 79, Fe, 20 00 Calc for $(CH_3NC)_4Fe(CN)_2$ C, 44 16 H, 4 42, N, 30 88 Fe 20 54 % Infra-red spectrum (KBr, μ) 3 32 (w) 3 39 (*w*) 4 56 (s) 4 76 (m) 6 93 (*m*) and 7 1 (*m*)

Synthesis of cyanopentakis(methyl isocyanide)iron (II) iodide

A sample of dicyanotetrakis(methyl isocyanide)iron (II) (15 8 g 58 1 mmole) was heated with a sample of methyl iodide (7 4 g, 52 2 mmole) in acetonitrile (100 ml) at 80–90° for 4 hr in a closed 320 ml stainless steel autoclave under autogenous pressure The resulting mass was evaporated to dryness under reduced pressure The solid was extracted with hot chloroform (150 ml) and the solution cooled to 0° Crystals of hexakis(methyl isocyanide)iron (II) iodide (m p 198) separated out and the product was identified by its infra-red spectrum The mother liquor yielded a further deposit of solid upon concentration and cooling It was purified by repeated crystallizations from hot chloroform Yield 70 per cent, m p 137–39° Found C, 30 61, H, 4 12, N, 19 35 I, 29 50, Fe 12 81 Calc for $(CH_3NC)_5Fe(CN)I\ H_2O$ C, 30 60, H, 3 93, N, 19 45, I, 29 42, Fe, 12 91% Infra-red spectrum (KBr, μ) 2 9 (*m*), 3 3 (*sh*), 3 4 (*w*), 3 9 (*w*), 4 51 (*s*), 4 67 (*m*), 5 3 (*w*) 6 2 (*w*) 6 93 (w) and 7 1 (*m*)

Conductivity measurements in nitrobenzene at 25° gave the following results

	Concentration (M)	Specific Conductance in Nitrobenzene (mho cm^{-1})
Cyanopentakis(methyl isocyanide) iron (II) iodide	10^{-4} molar	2 67 10 [illegible]
Cyanopentakis(benzyl isocyanide) iron (II) bromide	10^{-3} molar	2 58 10 [illegible](9)
Nitrobenzene		1 0 10 [illegible]

Transalkylation of methyl isocyanide complexes of iron with benzyl bromide

Five grammes (11 6 mmole) of cyanopentakis(methyl isocyanide)iron (II) iodide and 20 0 g (117 mmole) of benzyl bromide were heated in the presence of phenyl acetonitrile (40 ml) at 150–60° for 2 hr in a 300 ml R B flask, fitted with a dry ice-acetone trap through a reflux condenser Methyl bromide was liberated during the reaction and was collected in the trap The residual mass was evaporated to dryness under reduced pressure and the residue extracted with methyl ethyl ketone The resulting solution deposited a solid (3 1 g) upon concentration and cooling Yield – 40 per cent (Found C, 57 83, H, 4 42, N, 13 16 %) Test for iodine (as iodide) was positive Infra-red spectrum (KBr, μ) 3 3 (*w*), 3 4 (*w*), 4 56 (*vs*), 4 72 (*m*), 6 7 (*m*), 6 9 (*s*), 7 4 (*m*), 9 3 (*w*), 9 75 (*w*), 10 0 (*w*), 13 6 (*s*) and 14 35 (s) X-ray showed it as an amorphous compound

In another experiment, 17 3 g (34 8 mmole) of the hexakis(methyl isocyanide)iron (II) bromide and 85 g (498 mmole) of benzyl bromide were heated together in the presence of phenyl acetonitrile (100 ml) under the conditions as above The product was treated as before The methyl ethyl ketone extraction gave an insoluble product which was purified by crystallization from chloroform, m p 230 0–31 6° Found N, 14 52 Calc for $(C_6H_5CH_2NC)_4Fe(CN)_2$ N, 14 59% Infra-red spectrum (KBr, μ) 3 25 (*w*), 3 4 (*w*), 4 57 (*s*), 4 75 (*m*), 6 7 (*m*), 6 88 (*m*), 7 0 (*w*), 7 4 (*m*), 9 27 (*w*), 9 7 (*w*), 10 0 (*w*), 13 25 (*m*), 13 5 (*w*), 13 77 (*m*), 14 23 (*m*) and 14 4 (*w*)

The methyl ethyl ketone-soluble product was purified by recrystallization from methyl ethyl ketone, m p 106 0–10 8° Found N, 11 16 Calc for $(C_6H_5CH_2NC)_5Fe(CN)Br\ H_2O$ N, 10 98% Infra-red spectrum (KBr, μ) 2 9 (*m*), 3 3 (*w*), 3 42 (*w*), 4 57 (*s*), 4 74 (*m*), 6 2 (*w*) 6 3 (*w*) 6 73 (*s*), 6 92 (*s*), 7 46 (*s*), 8 1 (*w*), 8 38 (*w*), 8 7 (*w*), 9 3 (*m*), 9 72 (*m*), 10 0 (*w*) 10 25 (*w*), 10 4 (*w*), 10 96 (*w*), 12 2 (*w*), 13 35 (*m*), 13 7 (*s*), 14 27 (*s*) and 14 4 (*sh*) A total yield of 83 per cent was obtained for the combined products

X-ray diffraction data for the cyanopentakis(benzyl isocyanide)iron (II) bromide are given in Table 1

Nine grammes of dicyanotetrakis(methyl isocyanide)iron (II) was likewise treated with 30 0 g benzyl bromide in phenyl acetonitrile (100 ml) at 150 60° for 1½ hr in the manner described before The only species recovered was the dicyanotetrakis(benzyl isocyanide)iron (II) It was identified by means of its melting point (230°) and infra-red spectrum

TABLE 1 X-RAY DIFFRACTION DATA FOR $(C_6H_5CH_2NC)_5Fe(CN)Br\ H_2O$*

d (Å)	I/I_0	*d* (Å)	I/I_0
16 0	1 00	4 69	0 90
8 05	0 10	4 09	0 10
6 39	0 25	3 94	0 80
5 39	0 30	3 67	0 25
5 02	0 50	3 55	0 20
4 86	0 10	3 15	0 25

* These data were obtained using CuK_α radiation, Ni filter, tube voltage and current of 35 kV and 20 mA, and an exposure time of 6 hr Relative intensities were estimated visually

DISCUSSION

The results reported above show that the alkylation of potassium ferrocyanide with excess methyl bromide resulted in the formation of hexakis(methyl isocyanide) iron (II) bromide in high yield in accordance with the equation,

$$K_4Fe(CN)_6 + 6CH_3Br \rightarrow \underset{\mathrm{I}}{(CH_3NC)_6FeBr_2} + 4KBr \qquad (1)$$

I was characterized by its infra-red spectrum and chemical analysis The corresponding dicyanotetrakis(methyl isocyanide)iron (II) II was obtained by heating I under reduced pressure at or above 140°, whereupon methyl bromide was liberated and was identified by its boiling point

$$(CH_3NC)_6FeBr_2 \rightarrow \underset{\mathrm{II}}{(CH_3NC)_4Fe(CN)_2} + 2CH_3Br \qquad (2)$$

II was characterized by its infra-red spectrum and chemical analysis

The novel cyanopentakis(methyl isocyanide)iron (II) iodide III was synthesized by the alkylation of II with methyl iodide under controlled conditions Thus, III was *obtained in 70 per cent yield on heating II with methyl iodide (II $CH_3I = 1$ 1) at* 80-90 for 4 hr,

$$(CH_3NC)_4Fe(CN)_2 + CH_3I \rightarrow \underset{\text{III}}{(CH_3NC)_5Fe(CN)I} \quad (3)$$

together with the formation of some hexakis(methyl isocyanide)iron (II) iodide IV III was characterized by chemical analysis, melting point, infra-red spectrum, specific conductivity and X-ray diffraction It did not change in composition upon repeated crystallizations from chloroform It melted at 139 , while IV had a melting point of 198 and II decomposed without melting at 255 X-ray diffraction patterns of II, III and IV unambiguously identify them as three independent species III was found to be amorphous to X-rays while II and IV were crystalline Furthermore, specific conductivity measurement confirms III as univalent univalent electrolyte Molecular weight could not be determined due to dissociation (or association) of III in solution In experiments not reported here, the iodine in III was replaced by perchlorate and the resulting penta-methyl isocyanide complex did not change in composition upon crystallization Likewise, the dark brown cyanopentakis(methyl isocyanide)iron (II) triiodide was formed upon treating III with elemental iodine

All the three methyl isocyanide complexes readily underwent transalkylation reaction with benzyl bromide

$$(CH_3NC)_xFe(CN)_yX_z \quad xC_6H_5CH_2Br \rightarrow (C_6H_5CH_2NC)_xFe(CN)_yX_z + {}_xCH_3Br \quad (4)$$

The product obtained from III definitely contained the benzyl group (as evidenced by the infra-red spectrum), but the identity of the compound could not be ascertained The infra-red spectrum also showed the presence of isocyanide (4 56 μ) and cyanide (4 72 μ) groups It was amorphous to x-ray as was the original compound, III In contrast with the latter, which is an iodine salt, the bromide complex, I, as well as the covalent species, II, yielded products which were unambiguously characterized Thus, the reaction between I and excess benzyl bromide proceeded according to Equation (4) and the products were isolated and identified as dicyanotetrakis(benzyl isocyanide)iron (II) V and cyanopentakis(benzyl isocyanide)iron (II) bromide VI II, however, yielded only V Though the mechanism of the above reactions has not been investigated by the author, the observed products can be accounted for by the following sequence

$$\begin{tikzcd}
(CH_3NC)_6FeBr_2 \arrow[r, "\Delta"] \arrow[dd, "C_6H_5CH_2Br"] & (CH_3NC)_4Fe(CN)_2 \arrow[d, "C_6H_5CH_2Br"] \\
 & (C_6H_5CH_2NC)_4Fe(CN)_2 \arrow[d, shift left, "C_6H_5CH_2Br"] \\
(C_6H_5CH_2NC)_6FeBr_2 \arrow[r, "\Delta", "(9)"'] & (C_6H_5CH_2NC)_5Fe(CN)Br \arrow[u, shift left, "\Delta\ (9)"]
\end{tikzcd}$$

V and VI were characterized by means of melting points, mixed melting points (with samples prepared by independent routes),(9) chemical analyses, and infra-red spectra (identical with those of known pure compounds) VI was confirmed by its X-ray diffraction pattern, which was identical with that of the known compound

Acknowledgements—The author wishes to thank Drs H M HUBBARD and J A C ALLISON for many helpful suggestions

J. Inorg. Nucl. Chem. 1963 Vol. 25, pp. 975 to 983. Pergamon Press Ltd. Printed in Northern Ireland

ZINC CHLORIDE AND ZINC BROMIDE COMPLEXES—III

STRUCTURES OF SPECIES IN SOLUTION

D. F. C. Morris, E. L. Short and D. N. Waters
Department of Chemistry, Brunel College, London W.3

(Received 5 February 1963)

Abstract—Raman spectra of aqueous solutions containing zinc chloride or zinc bromide and of extracts into tri-n-butyl phosphate (TBP) have been obtained. The spectra are in agreement with a tetrahedral structure (T_d) for the ions $[ZnA_4]^{2-}$ (A = Cl, Br) and indicate that the molecules ZnA_2 have a linear configuration ($D_{\infty h}$) in both aqueous and TBP solutions. There is some evidence that the ions $[ZnA_3]^-$ have a planar triangular structure (D_{3h}). Probable arrangements are given for water and TBP molecules in the inner co-ordination sphere of the zinc atom in the various complexes.

In order to obtain further information on the structure and nature of zinc chloride and zinc bromide complexes in aqueous solutions and in extracts in tri-n-butyl phosphate (TBP), investigations have been made of their Raman spectra. Owing to the low intensity of Raman scattering, the measurements had to be carried out with rather concentrated solutions, but it appears that the results can be correlated with the properties of the complexes at low concentrations.$^{(1,2)}$

EXPERIMENTAL

Aqueous solutions. Suitable quantities of AnalaR zinc oxide were weighed out and dissolved in appropriate calculated quantities of hydrochloric acid or hydrobromic acid. AnalaR acids were used, hydrobromic acid was freshly distilled before use. In certain cases where it was desirable to have a relatively low halide concentration but to maintain an appreciable ionic strength, AnalaR perchloric acid was added.

The final solutions were either 1 M or 1.5 M in zinc, and were centrifuged and allowed to stand for a few hours in stoppered tubes to allow any suspended particles to settle before the Raman spectra were measured. Some solutions were prepared containing added sodium chloride or sodium bromide but in most cases any excess halide was added as hydrochloric acid or as hydrobromic acid.

Organic solvent and extracts. Tri-n-butyl phosphate was purified by the method of Alcock *et al.*$^{(3)}$ The dried compound was finally distilled under reduced pressure (b.p. 142° at 2–3 mm).

Organic extracts were prepared by equilibrating 10 ml of the appropriate aqueous solution containing zinc complexes with 10 ml of pure TBP at room temperature. Samples of TBP pre-treated with aqueous solutions with no zinc present were also prepared.

No difficulty was experienced from the formation of free halogens in the organic extracts. As the TBP solutions slowly undergo degradation,$^{(4,5)}$ spectra were taken shortly after their preparation.

---

(1) Part I. E. L. Short and D. F. C. Morris, *J. Inorg. Nucl. Chem.* **18**, 192 (1961).

(2) Part II. D. F. C. Morris and E. L. Short, *J. Chem. Soc.* 2662 (1962).

(3) K. Alcock, S. S. Grimley, T. V. Healy, J. Kennedy and H. A. C. McKay, *Trans. Faraday Soc.* **52**, 39 (1956).

(4) A. J. Moffat and R. D. Thompson, *J. Inorg. Nucl. Chem.* **16**, 365 (1961).

(5) A. S. Kertes and M. Halpern, *J. Inorg. Nucl. Chem.* **16**, 308 (1961); **19**, 359 (1961); **20**, 117 (1961).

Raman spectra The Raman spectra were measured both (a) photographically and (b) photoelectrically

(a) The photographic apparatus consisted of a Hilger Raman source-unit with mercury arc lamps and a Bellingham and Stanley direct-reading wavelength spectrometer with camera attachment The dispersion of the instrument was about 15 Å/mm in the region of the lines excited by Hg 4358 Å The volume of the Raman tube was ca 7 ml A concentrated solution of sodium nitrite was employed as a filter surrounding the sample tube For each solution spectra were photographed with exposure times up to 6 hr on Ilford SR-O blue-sensitive plates A copper arc spectrum was used as a standard for the measurement of frequencies of the Raman lines The estimated error in the observed $\Delta\bar{\nu}$ values is ca 4 cm^{-1} All the developed photographic plates were measured on a Hilger non-recording microphotometer In a number of cases both Stokes and anti-Stokes lines were observed to have been excited by Hg 4358 Å States of polarization could not be determined with this apparatus

(b) The photoelectric Raman spectrometer was designed and constructed in this Laboratory, and full details will be published elsewhere The double monochromator used as its dispersing elements two large 30 glass prisms in a Czerny-Turner arrangement Wavelength scanning was accomplished by mechanically rotating the two prism assemblies synchronously at a preset speed The emergent beam was allowed to fall on an E M I 9514S photomultiplier tube The output of this detector was amplified and the resulting direct current signal recorded on a Honeywell chart recorder Wavelength calibration was obtained by observing the line spectra of Hg, Na, Ar, He and the Raman spectrum of carbon tetrachloride

Exciting light from the Hg 4358 Å line was provided by a helical low pressure mercury lamp of the 'Toronto arc' type The lamp was water-cooled and was operated at ca 2 5 kW The interior of the casing surrounding the lamp was finished in white enamel to give high reflexion A vertical glass tube of rectangular section and of capacity ca 10 ml was used to contain the sample solutions The bottom of this cell consisted of a flat glass window through which the scattered light emerged into the optical system A concentrated solution of sodium nitrite was employed as a filter surrounding the sample tube Polarization studies were performed by inserting tubes of polaroid between the sample cell and the light-source

RESULTS AND DISCUSSION

Spectra of a number of aqueous solutions of zinc (II) containing varied concentrations of chloride showed three relatively intense polarized Raman lines at $\Delta\bar{\nu}$305, 286 and 275 cm^{-1} In the spectra of most of the solutions two of these strong lines were present, but at certain compositions, all three lines were present to some extent The intensities of the lines changed markedly as the ratio of total dissolved chloride to total zinc (II) was varied and it was apparent that the three lines arose from different zinc chloride complexes Raman spectra of TBP extracts from aqueous chloride solutions also showed lines of the same frequencies In addition, weak depolarized Raman lines were observed at 79 104 and 306 cm^{-1} in the spectra of certain aqueous solutions and TBP phases These lines were strongest in solutions containing a considerable excess of chloride

In the spectra of aqueous solutions containing zinc and bromide and of corresponding TBP extracts three relatively intense polarized Raman lines at 206, 182 and 172 cm^{-1} were observed The relative intensities of these lines one to another changed strikingly as the total bromide to total zinc concentration of solutions was varied Hence it was immediately apparent that the three lines arose from different chemical species Other much weaker depolarized lines at 66, 88 and 208 cm^{-1} were observed in aqueous solutions and organic extracts containing a considerable excess of bromide

Raman lines in the spectra of aqueous zinc halide solutions and TBP extracts were relatively sharp Some typical profiles are shown in Fig 1

Our assignments of the Raman lines are given in Table 1, which also lists conclusions of other workers Information from Parts I and II of this series was of assistance

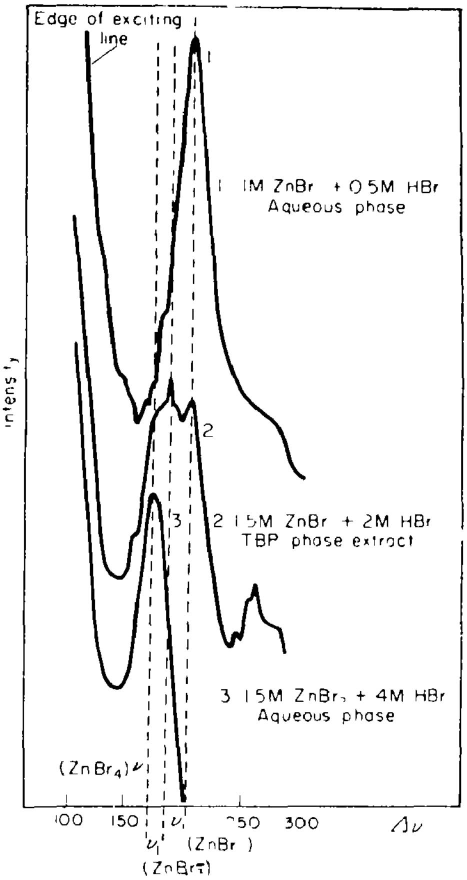


FIG. 1.—Raman spectra of solutions containing zinc bromide recorded photoelectrically.

TABLE 1.—OBSERVED RAMAN FREQUENCIES (cm^{-1}) AND THEIR ASSIGNMENT TO ZINC CHLORIDE AND ZINC BROMIDE SPECIES

Species	Present work	DELWAULLE[6]	KEÇKI and MANKOWSKI[7]
[ZnCl]			
$ZnCl_2$	**305**	**305**	**304**
$[ZnCl_3]^-$	**286**		
$[ZnCl_4]^{2-}$	**275**, 79, 104, 306	**282**, 82 116	**282**

Species	Present work	DELWAULLE[6]	YELLIN and PLANE[8]
$[ZnBr]^+$			**205**
$ZnBr_2$	**206**	**208**	**186**
$[ZnBr_3]$	**182**	**184**	
$[ZnBr_4]^{2-}$	**172**, 66, 88, 208	**172**, 61 82, 210	**172**, 63 81 213

Frequencies in Clarendon type refer to the symmetrical stretching mode to the interpretation of our spectra. Although the stability constants of Part I are valid only for an ionic strength of 0.691 M they do provide some indication of the relative proportions of different $[ZnA_j]^{(2-j)+}$ complexes (A = Cl,Br) in the aqueous solutions studied by Raman spectroscopy. Similarly, conclusions drawn in Part II as to the composition of zinc species which are extracted into TBP could be correlated with the spectral observations.

---

[6] M. L. DELWAULLE, *C. R. Acad. Sci., Paris* **240**, 2132 (1955); *Bull. Soc. Chim. France*, (**1955**), 1294.

[7] Z. KEÇKI and J. MANKOWSKI, *Roczniki Chem.* **36**, 375 (1962); Z. KEÇKI, *Spectrochim. Acta* **18**, 1165 (1962).

[8] W. YELLIN and R. A. PLANE, *J. Amer. Chem. Soc.* **83**, 2448 (1961).

It will be seen from Table 1 that the Raman lines observed by us correspond closely for the most part with those reported by other workers. However, there is a discrepancy between our assignment and that of YELLIN and PLANE[8] of the frequencies 206 (205) and 182 (186) cm^{-1} observed in the spectra of solutions containing zinc bromide complexes. This merits some comment at this stage. YELLIN and PLANE appear to base their assignments of the major Raman lines of Zn–Br complexes primarily on JOB plots. However, it apears to us difficult to measure the relative intensities of incompletely resolved Raman lines with sufficient accuracy to yield entirely unambiguous JOB plots. Moreover, the validity of the JOB method[9] for interpreting the composition of complexes has recently been shown to be questionable[10] in cases where, as here, there can be a change in stereochemistry between successive complexes. More positively, it is known from Part II of the present series that $[ZnBr]^+$ is extracted only to a negligibly small extent into TBP from aqueous solutions of hydrobromic acid. Yet the Raman line at 206 cm^{-1} appears with high intensity in the spectra of a number of TBP extracts. In addition we find that the variation in intensity of this line in the spectra of aqueous solutions containing a constant amount of zinc(II) and different amounts of total bromide matches the variation in intensity of the line in the spectra of corresponding TBP extracts, this implies that the line 206 cm^{-1} is due to analogous species in both phases.

Structure of the Zn^{2+} *aq ion*

We consider that the "free" ion Zn^{2+} in aqueous solution has six molecules of water arranged around it octahedrally forming a primary or inner hydration sphere. This conclusion is supported by a number of arguments, such as the following.

(a) Since Zn^{2+} has a completed 3*d*-subshell ($^1S_0$) and a spherical electronic charge distribution,[11] it may be expected to be surrounded symmetrically on average by water molecules in aqueous solution. A sixfold coordination of water molecules is to be expected on geometrical grounds if the radius ratio $r_{Zn^{2+}}/r_{H_2O}$ is the major factor determining the stereochemistry of the primary hydration sphere.

(b) The model for the structure of liquid water proposed by VAN PANTHALEON VAN ECK *et al.*[12] seems to favour six-co-ordination of water molecules around zinc ions. If the ions are visualized as occupying lattice points in the symmetrical octahedral structure of liquid water the energy change required to accommodate them should be a minimum.

---

[9] P. JOB, *Ann. Chim.* [10], **9**, 113 (1928).

[10] W. LIBUS, A. UGNIEWSKA and S. MINC, *Roczniki Chem.* **34**, 29 (1960).

[11] A. UNSOLD, *Ann. Phys.* **82**, 355 (1927).

[12] C. L. VAN PANTHALEON VAN ECK, H. MENDEL and W. BOOG, *Discuss. Faraday Soc.* **24**, 200 (1957); C. L. VAN PANTHALEON VAN ECK, H. MENDEL and J. FAHRENFORT, *Proc. Roy. Soc.* A **247**, 472 (1958).

(c) A large number of crystalline salt-hydrates(13) contain the group $[Zn\ 6H_2O]^{2+}$

(d) An interpretation of the enthalpies of hydration of divalent ions of the First Transition Series from the standpoint of the ligand-field theory is possible on the basis that the ions are octahedrally coordinated in water (14) The same criterion applies to the interpretation of spectroscopic and magnetic data for the hydrated ions (15)

Structure of the species $[ZnA]^+$ *aq*

We could identify no definite Raman lines in the spectra of aqueous solutions of stocheiometric composition (a) M $ZnClClO_4$ (b) M $ZnBrClO_4$ apart from lines attributable to ClO_4^- One would expect from stability constants(1) that such solutions should contain a considerable proportion of the ions $[ZnA]^+$ In particular the virtual absence of a line at 206 cm^{-1} in the spectrum of (b) is further evidence against the assignment of this line to $[ZnBr]^+$ by Yellin and Plane We conclude that the zinc halogen interaction in $[ZnA]^+$ is probably essentially ionic, since Woodward and coworkers(16) have deduced that the intensity of the Raman effect for an electrostatic ion pair would be at least a hundred times weaker than that resulting from a covalent bond

From a comparison of values of the standard partial molal entropies S_0 derived from Cobble's(17) empirical equation for the ions $[CdCl]^+$, [CdBr] and $[CdI]^+$ in aqueous solution with observed values for S_0, it appears that the halide replaces one water molecule from the hydration shell of the Cd^{2+} cation in the association reaction (18) Also on the basis of X-ray measurements Van Panthaleon Van Eck(19) has proposed that the ion $[HgCl]^+$ aq possesses sixfold coordination $[HgCl\ 5H_2O]^+$ By comparison it may be suggested that the formation of the complexes $[ZnA]^+$ aq involves the replacement of one water molecule of $[Zn\ 6H_2O]^{2+}$ by a halide ion

Structures of the species ZnA_2

The strongly polarized Raman line $\Delta\bar{\nu} = 305\ cm^{-1}$ observed in the spectra of aqueous solutions containing chloride and zinc II in the concentration ratios ca 1 5–4 5 and in the spectra of corresponding TBP extracts is assigned to the symmetric vibration of linear Cl Zn Cl Similarly the frequency 206 cm^{-1} observed in the spectra of a number of aqueous zinc bromide solutions (total Br/total Zn ca 1 5 4) and TBP extracts we attribute to linear Br-Zn-Br

We propose that in these species in aqueous solution the zinc atom possesses octahedral coordination, with two covalent Zn A bonds and four Zn OH_2 contacts This is similar to the stereochemical arrangement proposed for $HgCl_2$ aq on the basis of X-ray diffraction measurements (19)

---

(13) A F Wells *Structural Inorganic Chemistry*, (3rd Ed) Clarendon Press, Oxford (1962)

(14) J S Griffith and L E Orgel, *Quart Rev* **9**, 381 (1957), P George and D S McClure *Progr Inorg Chem* **1**, 381 (1959)

(15) C K Jorgensen, *Absorption Spectra and Chemical Bonding in Complexes* Pergamon, Oxford (1962) T M Dunn, *Modern Coordination Chemistry*, (Edited by J Lewis and R G Wilkins) p 229 Interscience, New York (1960), N Figgis and J Lewis, *Ibid* p 400

(16) J H B George, J A Rolfe and L A Woodward, *Trans Faraday Soc* **49**, 375 (1953)

(17) J W Cobble, *J Chem Phys* **21**, 1446 (1953)

(18) J M Austin, R A Matheson and H N Parton, *The Structure of Electrolytic Solutions*, (Edited by W J Hamer) p 365 Wiley, New York (1959)

(19) C L Van Panthaleon Vak Eck, Thesis, Leiden (1958)

It seems likely that the complexes $ZnA_2 \cdot 2TBP$ present in TBP extracts$^{(2)}$ have associated water molecules.$^{(20)}$ In these complexes the zinc atom again probably has co-ordination number six with two Zn–A covalent bonds, two Zn   OP(OBu)$_3$ contacts and two Zn   OH$_2$ contacts.

Structures of the species $[ZnA_4]^{2-}$

The tetrahedral structure of the ions $[ZnCl_4]^{2-}$ and $[ZnBr_4]^{2-}$ in crystalline compounds has been established by various workers (e.g. see MOROSIN and LINGAFELTER$^{(21)}$). From the Raman spectra of aqueous solutions and TBP extracts containing excess of halide the following lines can be assigned to the species $[ZnCl_4]^{2-}$ and $[ZnBr_4]^{2-}$.

$[ZnCl_4]^{2-}$	$\Delta\bar{\nu}$(cm^{-1})	79	104	275	306
$[ZnBr_4]^{2-}$	$\Delta\bar{\nu}$(cm^{-1})	66	88	172	208
Intensity		Strong	Strong	Very strong	Rather weak
Polarization		Depolarized	Depolarized	Strongly polarized	Depolarized
Assignment		$\nu_2(E)$	$\nu_4(F_2)$	$\nu_1(A_1)$	$\nu_3(F_2)$

These were the only lines attributable to zinc halide complexes that could be observed in the spectra of aqueous solutions containing a (total halide/total zinc) ratio of ten and of corresponding TBP extracts.

The number of observed frequencies and the states of polarization provide strong evidence that the species $[ZnA_4]^{2-}$ possess regular tetrahedral structure (point group T_d) in solution.

The fact that Raman frequencies characteristic of $[ZnCl_4]^{2-}$ and $[ZnBr_4]^{2-}$ are observed in the spectra of TBP extracts shows that the acido-species $H_2ZnA_4 \cdot 2TBP$ must be regarded as associated electrolytes. By analogy with the results of physico-chemical studies of the extraction of mineral acids into TBP$^{(22)}$ it appears that the species may be formulated as $[H \cdot TBP \cdot 3H_2O]_2^{+}$ $[ZnA_4]^{2-}$.

Structures of the species $[ZnA_3]^-$

It is clear from stability constants$^{(1)}$ that $[ZnCl_3]^-$ can only be investigated in aqueous solution in the presence of appreciable amounts of the complexes $ZnCl_2$ or $[ZnCl_4]^{2-}$. However, a strong polarized line at 286 cm^{-1} could be detected in the spectra of certain aqueous solutions and corresponding TBP extracts and was assigned to $[ZnCl_3]^-$. Among the spectra of aqueous solutions studied the line was of highest intensity in the spectrum of a solution with a (total chloride/total zinc) ratio of 3:2. This line was very intense in the spectrum of a TBP extract from this aqueous solution and could be detected in extracts from aqueous solutions with a (total chloride/total zinc) ratio varying from ca. 2.5 to 4.5. Two lines at 236 and 348 cm^{-1} which could possibly be assigned to $[ZnCl_3]^-$ seemed to be present in some of the spectra. However, these lines were so weak that they could possibly have been confused with background fluctuation.

---

(20) B. V. NEKRASSOV and V. V. OVSKYANKINA, *J. Gen. Chem. U.S.S.R.* **11**, 573 (1941); H. IRVING and F. J. C. ROSSOTTI, *J. Chem. Soc.* 1927 (1955).

(21) B. MOROSIN and E. C. LINGAFELTER, *Acta Cryst.* **12**, 611, 744 (1959).

(22) A. S. KERTES, *J. Inorg. Nucl. Chem.* **14**, 104 (1960); A. S. KERTES and V. KERTES, *Canad. J. Chem.* **38**, 612 (1960); E. FOA, N. ROSINTAL and Y. MARCUS, *J. Inorg. Nucl. Chem.* **23**, 109 (1961).

The line at 182 cm^{-1} observed in the spectra of a number of aqueous solutions and TBP extracts containing zinc bromide complexes (Br_{tot}/Zn_{tot} ca 2-7 5) was assigned to $[ZnBr_3]^-$ and is presumably the ν_1 fundamental vibration frequency It was not possible to identify any other Raman lines of this species

The similarity in solvent extraction behaviour of trichlorozincate and tribromozincate reported in Part II suggests that in solution $[ZnBr_3]^-$ is structurally similar to $[ZnCl_3]^-$ We propose the structure I shown in Fig 2 for these ions in solution This conclusion is supported by a number of considerations, such as the following

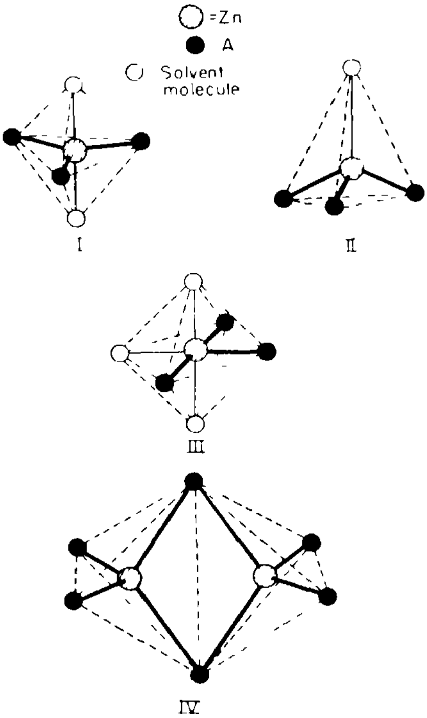


Fig 2—Possible structures for a species ZnA_3 in solution IV is a possible structure of a dimer I is the structure most in accord with available evidence

(a) The $ZnCl_3$ part of structure I in Fig 2 would be expected to give rise to three Raman lines (one polarized), whereas II would give rise to four lines (two polarized), III would yield six lines (three polarized) and IV nine lines (four polarized) (23)

(b) Structure I is the most likely on the basis of minimization of halide–halide repulsions

(c) Successive step-formation constants $K_j = [ML_j]/[ML_{j-1}][L]$ of a series of mononuclear complexes formed by a metal ion M and identical ligands L in aqueous solution usually decrease in magnitude This may be expected from considerations of statistics, steric factors and, for charged ligands, of coulombic interaction (24) Moreover, values of log (K_j/K_{j+1}) are usually positive and approximately equal (25)

---

(23) L A Woodward, *Quart Revs* **10**, 185 (1956)

(24) J Bjerrum, *Metal Ammine Formation in Aqueous Solution* Haase, Copenhagen (1941)

(25) C L Van Panthaleon Van Eck, *Rec Trav Chim* **72**, 529 (1953)

Exceptions to this behaviour may occur if the successive complexes do not possess similar stereochemistry (although other factors which may cause anomalies are a change in the ground state of the metal ion, π bonding, or steric hindrance)[26] Some plots of log K_j against $(j-1)$ are shown in Fig 3, and it might be inferred from these that the ions $[ZnA_3]^-$ aq are of different structure type from ZnA_2 aq (octahedral) and $[ZnA_4]^{2-}$ aq (tetrahedral) This would favour the acceptance of structure I rather than structures II and III in Fig 2 for $[ZnCl_3]^-$ or $[ZnBr_3]^-$ in aqueous solution

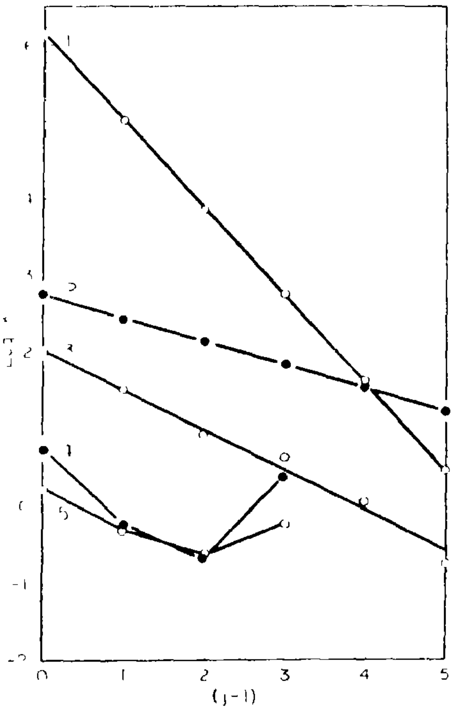


FIG 3 Log K_j as a function of $(j-1)$ for (1) $[AlF_j]^{(3-j)+}$, (2) $[Ni(N_2H_4)_j]^{2+}$, (3) $[Co(NH_3)_j]^{2+}$, (4) $[ZnCl_j]^{(2-j)+}$, (5) $[ZnBr_j]^{(2-j)+}$

(d) Structure I in Fig 2 is similar to that proposed by VAN PANTHALEON VAN ECK[19] for $[HgCl_3]^-$aq on the basis of X-ray diffraction measurements It is also relevant to note that according to BRODERSEN and RUDORFF[27] the compound Hg_2NHBr_2 should be formulated as $[Hg_4(NH)_2]^{2+}$ $[Br]^-$ $[HgBr_3]^-$, the $[HgBr_3]^-$ ion having a triangular planar configuration

(e) The number of TBP molecules associated with complexes containing $[ZnBr_3]^-$[2] is in accord with structure I in Fig 2 and is not compatible with the other structures

CONCLUSIONS

It appears that minimization of halide-halide repulsions is a major factor determining the shapes of zinc chloride and zinc bromide complexes

---

[26] F J C ROSSOTTI, *Modern Co-ordination Chemistry*, (Edited by J LEWIS and R G WILKINS) p 1 Interscience, New York (1960)

[27] K BRODERSEN, *Acta Cryst* **8**, 723 (1955), K BRODERSEN and W RUDORFF, *Z Naturforsch* **9 B**, 164 (1954)

The change in co-ordination number from six in $[Zn\,6H_2O]^{2+}$ to four in $[ZnA_4]^{2-}$ can be correlated with PAULING's electroneutrality principle. According to this principle(28) stable complexes are those with structures such that each atom has only a small electric charge approximating to zero (that is, in the range −1 to +1). Since Cl^- and Br^- are more polarizable than H_2O*, a suitable reduction in the charge of Zn^{2+} from its formal value of +2 may be expected from the co-ordination of fewer Cl^- or Br^- ions than H_2O molecules. An alternative explanation of the preferred co-ordination numbers with the different ligands can be obtained from the orbital contraction theory of CRAIG and MAGNUSSEN(31) (see NYHOLM(32)).

Acknowledgements—The authors are grateful to Messrs. Hilger and Watts Limited for the loan of a Raman source unit. They are indebted to Dr. P. L. GOGGIN for helpful correspondence.

---

* Electronic polarizabilities of Cl^- and Br^- are 3.53 and 4.97 Å^3, respectively, according to FAJANS and JOOS.(29) Corresponding magnitudes due to PAULING(30) are 3.66 and 4.77 Å^3. The polarizability of H_2O is 1.48 Å^3.

(28) L. PAULING, *J. Chem. Soc.* (**1948**), 1461; *The Nature of the Chemical Bond* (3rd Ed.) Cornell Univ. Press, New York (1960).

(29) K. FAJANS and G. JOOS, *Z. Phys.* **23**, 388 (1924).

(30) L. PAULING, *Proc. Roy. Soc.* A **114**, 191 (1927).

(31) D. P. CRAIG and E. A. MAGNUSSEN, *J. Chem. Soc.* 4895 (1956); *Discuss. Faraday Soc.* **26**, 116 (1958).

(32) R. S. NYHOLM, *Proc. Chem. Soc.* 273 (1961).

J Inorg Nucl Chem 1963, Vol 25 pp 985 to 993 Pergamon Press Ltd Printed in Northern Ireland

THERMAL DECOMPOSITION OF METAL COMPLEXES—VI SOME AMMINE COBALT (II) COMPLEXES(1)

W W Wendlandt and J P Smith
AFOSR Center for Molecular Research, Department of Chemistry,
Texas Technological College, Lubbock, Texas

(*Received* 27 *December* 1962, *in revised form* 15 *February* 1963)

Abstract—The thermal dissociation of a number of cobalt (II) ammine complexes of the type, $[Co(NH_3)_6]X_2$ (X = Cl, Br, I, and NO_3), and $[Co(NH_3)_5]SO_4$, were studied by thermogravimetry differential thermal analysis, and gas evolution analysis The thermal dissociation of these complexes involved intermediate ammine complexes containing lower ammonia to cobalt ratios For the chloride and bromide complexes, the dissociation sequence was $[Co(NH_3)_6]X_2 \rightarrow [Co(NH_3)_2]X_2 \rightarrow [Co(NH_3)]X_2 \rightarrow CoX_2$ The stoichiometry of the dissociation of $[Co(NH_3)_6](NO_3)_2$ was $9[Co(NH_3)_6](NO_3)_2 \rightarrow 3Co_3O_4 + 30NH_3 + 36H_2O + 17N_2 + 4NO + 2N_2O$

The thermal dissociation of the hexammines of the cobalt (II) halides and sulphate has been the subject of a number of investigations The hexamminecobalt (II) chloride and bromide lose four moles of ammonia per mole of complex when heated, to yield the diammines, $[Co(NH_3)_2X_2]$(X = Cl, Br) (2–6) Two forms of the diammines were obtained, a thermally unstable purple coloured β-form (trans-) and a stable pink coloured α-form (cis-) Upon further heating, the diammines yielded the respective monoammines and then the anhydrous cobalt (II) halides (5)

Similarly, hexamminecobalt (II) iodide thermally decomposes to the diammine which exists in an unstable malachite green coloured β-form and a stable blue coloured γ-form (3,5–7) Further heating gives cobalt (II) iodide rather than the monoammine as in the case of the other halide complexes

The thermal dissociation of the pentamminecobalt (II) sulphate gives $[Co(NH_3)_4]SO_4$ at 106–116°, $[Co(NH_3)_2]SO_4$ at 254°, and $[Co(NH_3)_{0.5}]SO_4$ between 254 and 257° (5,8) There is also reported that a triammine can be prepared by heating $[Co(NH_3)_5]SO_4$ at 133° (8)

In connection with our studies on the thermal dissociation of the $[Co(NH_3)_6]X_3$(9) and $[Co(NH_3)_5X]X_2$(10) complexes, it was of interest to investigate the thermal dissociation of the $[Co(NH_3)_6]X_2$ (X = Cl, Br, I, and NO_3) and $[Co(NH_3)_6]SO_4$ complexes. The compounds were studied by the techniques of differential thermal analysis (DTA), thermogravimetric analysis (TGA), and gas evolution analysis (GE).

---

(1) For Part (V) see W W Wendlandt and J P Smith *J Inorg Nucl Chem* **25**, 843 (1963)

(2) F Rose, *Untersuchungen uber ammoniakalische kobalt verbindungen* Heidelberg **26**, (1871)

(3) W Biltz and B Fetkenheuer, *Z Anorg chem* **89**, 97 (1914)

(4) A Naumann and J Rili, *Ber Chem Dtsch Ges* **42**, 3792 (1909)

(5) G L Clark, A J Quick and W D Harkins, *J Amer Chem Soc* **42**, 2483 (1920)

(6) G L Clark and H K Buckner, *J Amer Chem Soc* **44**, 230 (1922)

(7) C F Rammelsberg, *Pogg Ann* **48**, 155 (1839)

(8) F Ephriam, *Z Phys Chem* **83**, 196 (1915)

(9) W W Wendlandt, *J Inorg Nucl Chem* **25**, 545 (1963)

(10) W W Wendlandt and J P Smith, *J Inorg Nucl Chem*, In press

EXPERIMENTAL

Thermobalance. The automatic recording thermobalance has previously been described.(11) Sample sizes ranged in weight from 50 to 100 mg. The complexes were pyrolysed in a static air atmosphere at an atmospheric pressure of about 680 mm. The furnace heating rate was about 5°C per min.

Differential thermal analysis-gas evolution apparatus. The apparatus used has previously been described.(12) Sample sizes ranged in weight from 50-60 mg. The heating rate was about 10°C per min.

TABLE 1. ANALYSES OF COBALT (II) AMMINE COMPLEXES

Compound	Cobalt (%) Theor	Cobalt (%) Found	Ammonia (%) Theor	Ammonia (%) Found
$[Co(NH_3)_6]Cl_2$	25.40	25.9	44.04	44.1
cis-$[Co(NH_3)_2]Cl_2$	35.96	35.8	20.78	20.3
trans-$[Co(NH_3)_2]Cl_2$	35.96	35.5	20.78	21.0
$[Co(NH_3)]Cl_2$	40.13	42.0	11.59	10.3
$[Co(NH_3)_6]Br_2$	18.36	18.5	31.84	31.7
cis-$[Co(NH_3)_2]Br_2$	23.31	23.4	13.47	13.8
trans-$[Co(NH_3)_2]Br_2$	23.31	23.0	13.47	13.0
$[Co(NH_3)]Br_2$	25.00	25.8	7.22	6.84
$[Co(NH_3)_6]I_2$	14.20	14.2	24.62	24.8
cis-$[Co(NH_3)_2]I_2$	16.99	16.8	9.82	9.9
trans-$[Co(NH_3)_2]I_2$	16.99	16.0	9.82	10.0
$[Co(NH_3)_6](NO_3)_2$	20.67	20.8	35.84	36.1
$[Co(NH_3)_4](NO_3)_2$	23.47	23.0	27.13	27.3
$[Co(NH_3)_6]SO_4$	22.92	23.3	39.73	41.3
$[Co(NH_3)_4]SO_4$	26.41	25.8	30.53	30.2
$[Co(NH_3)_{0.5}]SO_4$	36.05	36.3	5.21	5.3

Preparation of complexes. The complexes, $[Co(NH_3)_6]X_2$ (X = Cl, NO_3) and $[Co(NH_3)_6]SO_4$, were prepared by reacting gaseous ammonia with methanol suspensions of the salts as previously described.(5) The rose coloured precipitates were filtered off and dried at 80° in an atmosphere of ammonia.

The complexes, $[Co(NH_3)_6]X_2$ (X = Br and I) were prepared by adding concentrated HBr and HI to a concentrated aqueous solution of cobalt (II) chloride, neutralizing with ammonium hydroxide, and cooling. The crystals were collected and dried as described above.

The intermediate ammine complexes, β-$[Co(NH_3)_2]X_2$ (X = Cl, Br, I), $[Co(NH_3)_4]SO_4$, and $[Co(NH_3)_4](NO_3)_2$ were prepared by heating the hexammines *in vacuo* at 100° for 24 hr. The complex, $[Co(NH_3)]_{0.5}SO_4$, was prepared by heating the hexammine *in vacuo* at 275° for 24 hr.

The nitrate complex was analyzed for cobalt by ignition in air at 800° and weighing as Co_3O_4. The other complexes were analyzed for cobalt by ignition of the compounds in helium and weighing as the anhydrous salts. The ammonia was determined by the Kjeldahl method. The results of the analytical determinations are given in Table 1.

---

(11) W. W. WENDLANDT, T. D. GIORGE, K. V. KRISHNAMURTY, *J. Inorg. Nucl. Chem.* **21**, 69 (1961).

(12) W. W. WENDLANDT, *Analyt. Chim. Acta* **27**, 309 (1962).

RESULTS AND DISCUSSION

Weight-loss studies The weight-loss curves for the cobalt (II) ammine complexes are given in Fig 1 while the weight-loss data are given in Table 2.

The weight-loss curves indicated that all of the compounds began to evolve ammonia in the 80-90° temperature range Intermediate ammines, as indicated from

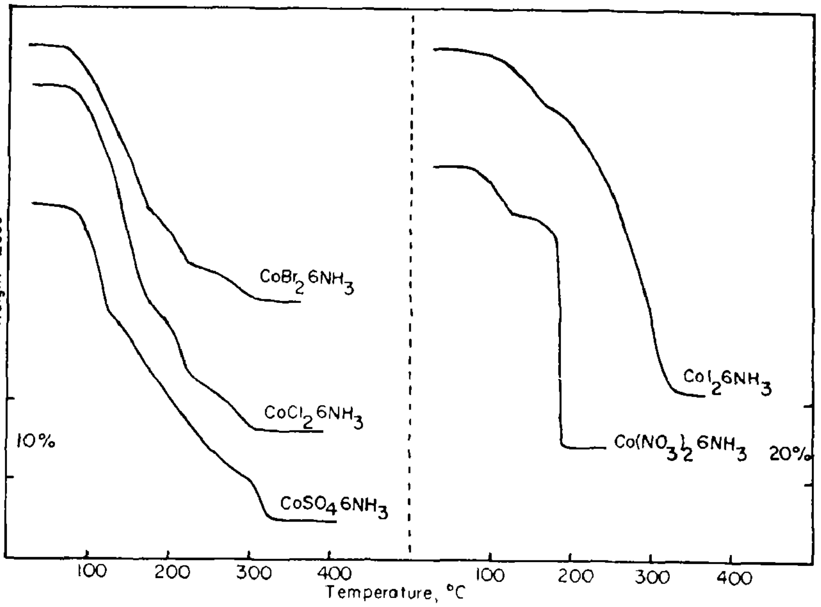


FIG 1 - Weight-loss curves of ammine complexes

TABLE 2 —WEIGHT-LOSS DATA FOR COBALT (II) AMMINE COMPLEXES

Compound	Weight-loss (%)					
	$[Co(NH_3)_2]X_2$		$[Co(NH_3)]X_2$		CoX_2	
	Theor	Found	Theor	Found	Theor	Found
	180°C		220		302	
$[Co(NH_3)_6]Cl_2$	29.36	28.2	36.70	36.0	44.04	43.8
	178		219		300	
$[Co(NH_3)_6]Br_2$	21.22	20.4	26.53	26.2	31.84	31.8
	192				315	
$[Co(NH_3)_6]I_2$	16.42	16.5			24.62	80.7
	$[Co(NH_3)_4](NO_3)_2$				Co_3O_4	
	125°				185	
$[Co(NH_3)_6](NO_3)_2$	11.95	11.9			71.85	71.0
	$[Co(NH_3)_4]SO_4$		$[Co(NH_3)_{0.5}]SO_4$		$CoSO_4$	
	113		303		321	
$[Co(NH_3)_6]SO_4$	13.24	14.1	36.42	35.6	39.73	41.5

breaks in the weight-loss curve, were found for $[Co(NH_3)_6]Cl_2$, $[Co(NH_3)_6]Br_2$, $[Co(NH_3)_6]I_2$, and $[Co(NH_3)_6](NO_3)_2$. However, the first two complexes gave three breaks in the curve while the last two had only two. The nitrate complex, due to the presence of reducing (ammonia) and oxidizing (nitrate) groups, exploded at about 180°.

The weight-loss curves for $[Co(NH_3)_6]Cl_2$ and $[Co(NH_3)_6]Br_2$ were similar to each other. Curve breaks at 178–180° indicated the compositions, $[Co(NH_3)_2]Br_2$ and $[Co(NH_3)_2]Cl_2$, respectively. Other curve breaks at 219–200° indicated the presence of the monoammines $[Co(NH_3)]Br_2$ and $[Co(NH_3)]Cl_2$, while the anhydrous salt horizontal weight levels were obtained in the 300–302° temperature range. Thus, the thermal dissociation sequence appears to be (where X = Cl and Br)

$$[Co(NH_3)_6]X_2 \xrightarrow{80} [Co(NH_3)_2]X_2 + 4NH_3$$

$$[Co(NH_3)_2]X_2 \xrightarrow{150} [Co(NH_3)]X_2 + NH_3$$

$$[Co(NH_3)]X_2 \xrightarrow{220} CoX_2 + NH_3$$

The weight-loss curve for $[Co(NH_3)_6]I_2$ had only a rather indefinite break at 195°. The stoichiometry of the compound formed at this temperature, as calculated from weight-loss data, was that of $[Co(NH_3)_2]I_2$. Above this temperature there was no evidence for the formation of any other intermediate ammines nor of the anhydrous CoI_2. Instead of CoI_2 as shown by Table 1, the oxide, Co_3O_4, was obtained at 315°. This is probably due to the oxidation reaction

$$3[Co(NH_3)_2]I_2 + 2O_2 \xrightarrow{195} Co_3O_4 + 3I_2 + 6NH_3$$

This reaction is substantiated by the data for the weight-loss to the oxide: 80.66 per cent theor., 80.7 per cent found.

The weight-loss curve for $[Co(NH_3)_6](NO_3)_2$ showed that two moles of ammonia per mole of complex were evolved, giving a break in the curve at 125° which corresponded to the stoicheiometry, $[Co(NH_3)_4](NO_3)_2$. On further heating, the tetrammine exploded at 180°, giving a residue of Co_3O_4.

The weight-loss curve for $[Co(NH_3)_6]SO_4$ gave no well defined breaks as was found for the other compounds. The curve break at 113° approximated the composition, $[Co(NH_3)_4]SO_4$, while the break at 303° approximated that for $[Co(NH_3)_{0.5}]SO_4$, however, these compositions might be fortuitous. The anhydrous salt, $CoSO_4$, was obtained at 340°.

Differential thermal analysis–gas evolution studies. The DTA curves of the ammine complexes are given in Figs. 2–4 while the GE curves are given in Figs. 5 and 6.

The DTA curves for the various $[Co(NH_3)_n]Cl_2$ complexes, Fig. 2, showed evidence for the formation of the diammines and monoammines, as previously indicated by the weight-loss curves. The origin of the various endothermic peaks was determined by obtaining the DTA curves of authentic lower ammine complexes.

The DTA curve for $[Co(NH_3)_6]Cl_2$ had three endothermic peaks, with peak maxima temperatures, henceforth referred to as peak temperatures, of 143°, 231°,

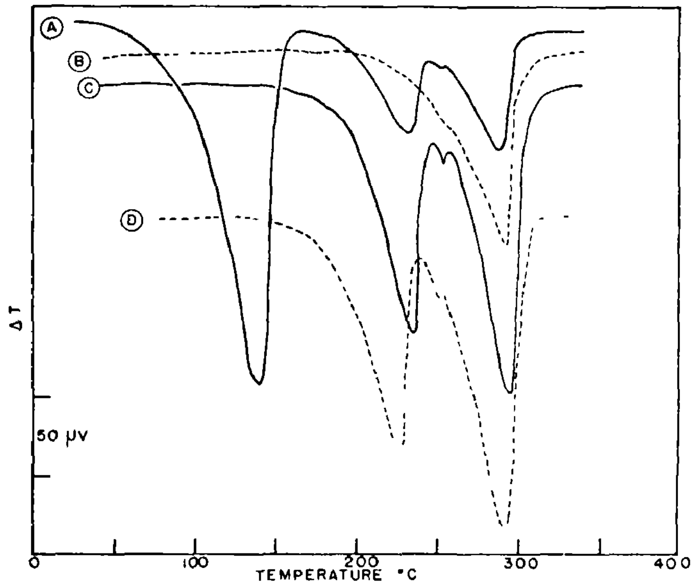


FIG. 2 Differential thermal analysis curves of ammine complexes
A $[Co(NH_3)_6]Cl_2$, *B* $[Co(NH_3)]Cl_2$, *C* *cis*-$[Co(NH_3)_2]Cl_2$,
D *trans*-$[Co(NH_3)_2]Cl_2$

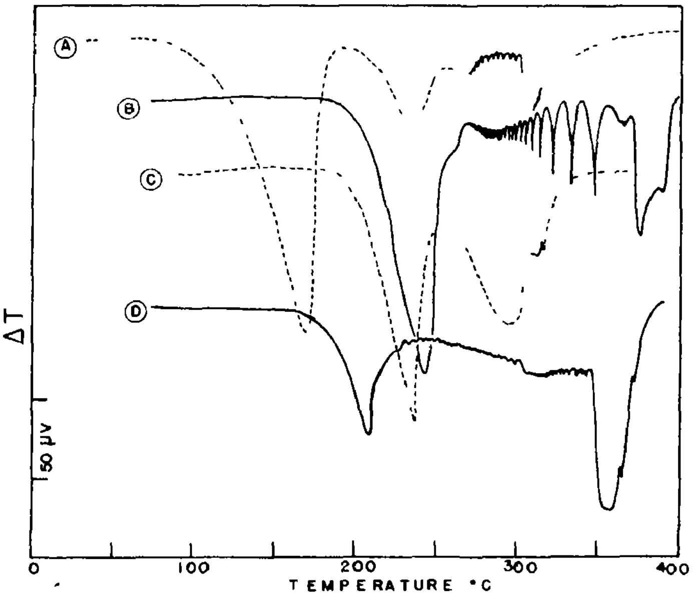


FIG 3 —Differential thermal analysis curves of ammine complexes
A $[Co(NH_3)_6]Br_2$, *B* *cis*-$[Co(NH_3)_2]Br_2$, *C* *cis*-$[Co(NH_3)_2]Br_2$ and Al_2O_3,
D $[Co(NH_3)]Br_2$

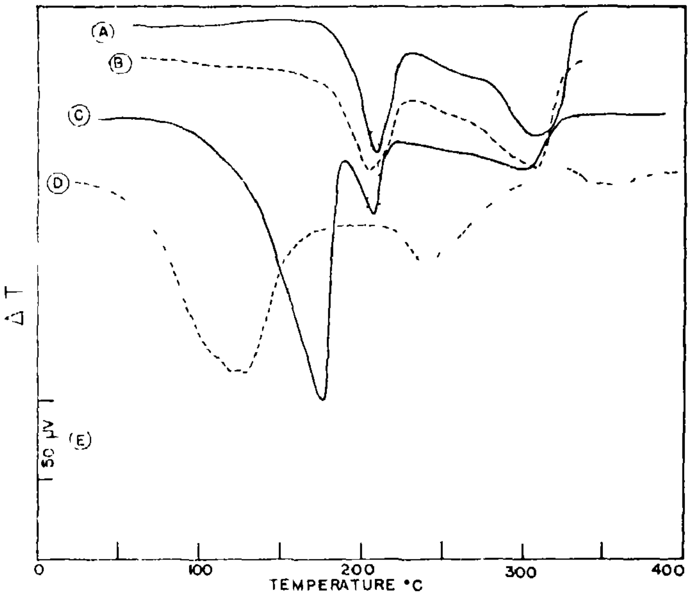


FIG 4 Differential thermal analysis curves of ammine complexes
A *cis*-$[Co(NH_3)_2]I_2$, *B* *trans*-$[Co(NH_3)_2]I_2$, *C* $[Co(NH_3)_6]I_2$
D $[Co(NH_3)_6]SO_4$, *F* $[Co(NH_3)_6](NO_3)_2$

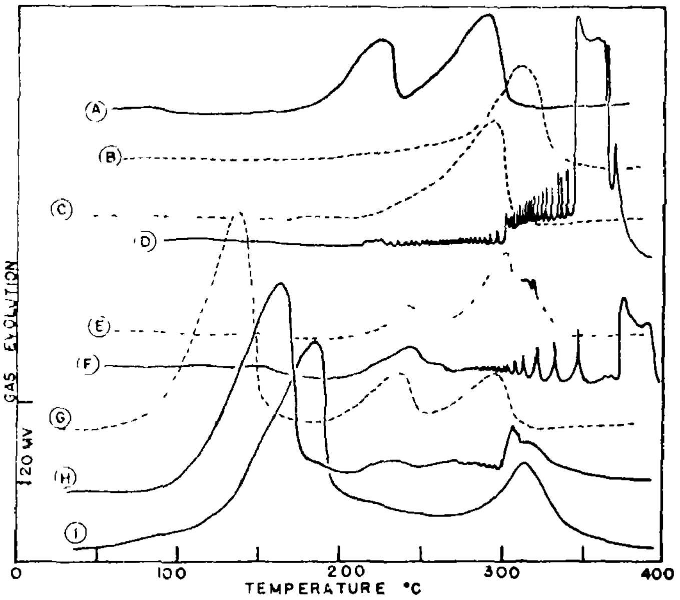


FIG 5 Gas evolution curves of ammine complexes
A *trans*-$[Co(NH_3)_2]Cl_2$, *B* *cis*-$[Co(NH_3)_2]Cl_2$, *C* $[Co(NH_3)]Cl_2$, *D* $[Co(NH_3)]Br_2$,
E *cis*-$[Co(NH_3)_2]Br_2$ and Al_2O_3, *F* *cis*-$[Co(NH_3)_2]Br_2$, *G* $[Co(NH_3)_6]Cl_2$,
H $[Co(NH_3)_6]Br_2$, *I* $Co[(NH_3)_6]I_2$

and 286°, respectively On the basis of the DTA curves for *cis*- and *trans*-$[Co(NH_3)_2]Cl_2$ and $[Co(NH_3)]Cl_2$, the assignment for these peaks is as follows

(a) 143° endothermic peak

$$[Co(NH_3)_6]Cl_2 \rightarrow [Co(NH_3)_2]Cl_2 + 4NH_3$$

(b) 231° endothermic peak

$$[Co(NH_3)_2]Cl_2 \rightarrow [Co(NH_3)]Cl_2 + NH_3$$

(c) 286° endothermic peak

$$[Co(NH_3)]Cl_2 \rightarrow CoCl_2 + NH_3$$

There was a slight shift in peak temperature for the first peak in the curves for *cis*- and *trans*-$[Co(NH_3)_2]Cl_2$ The *cis*- peak temperature was 234 in contrast to the *trans*-peak temperature of 227° The second peak temperatures however were much closer together, at 293° and 290°, respectively

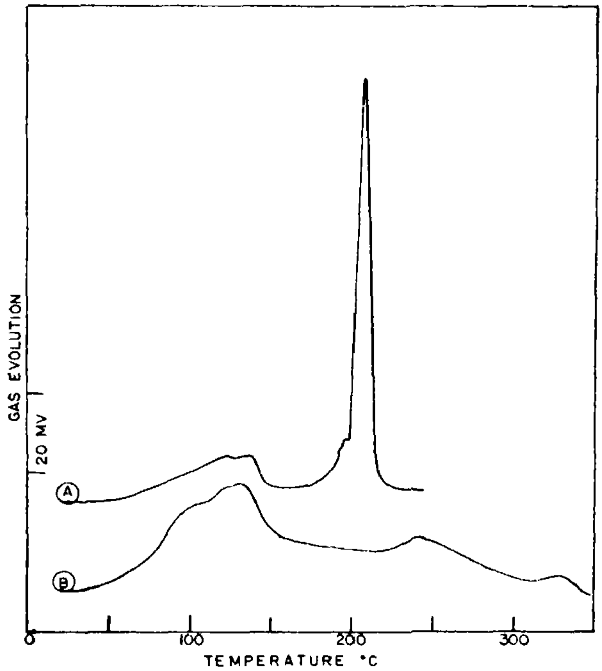


FIG 6 —Gas evolution curves of ammine complexes
A $[Co(NH_3)_6](NO_3)_2$, *B* $[Co(NH_3)_6SO_4$

All of the GE curves for the cobalt (II) chloride ammines had peaks at the same temperatures as the peaks found in the DTA curves This indicated that all of the reactions found in the DTA curve resulted in the evolution of a gaseous product

The DTA curves for the $[Co(NH_3)_n]Br_2$ complexes, Fig 3, were similar to those obtained for the $[Co(NH_3)_n]Cl_2$ complexes The curves were complicated by the fusion of the ammine complexes at temperatures above 200° This resulted in a system containing *liquid* → *gaseous* state equilibria which gave many small endothermic peaks in the curve

The DTA curve of $[Co(NH_3)_6]Br_2$ gave three major endothermic peaks with peak temperatures of 168°, 233°, and 308°, respectively Also present was a smaller shoulder peak at about 265 From the curves for *cis*-$[Co(NH_3)_2]Br_2$ and $[Co(NH_3)]Br_2$, the assignment for these peaks is as follows

(a) 168° endothermic peak

$$[Co(NH_3)_6]Br_2 \rightarrow [Co(NH_3)_2]Br_2 + 4NH_3$$

(b) 233 endothermic peak

$$[Co(NH_3)_2]Br_2 \rightarrow [Co(NH_3)]Br_2 + NH_3$$

(c) 308 endothermic peak

$$[Co(NH_3)]Br_2 \rightarrow CoBr_2 + NH_3$$

From the erratic behaviour of the curve above 260°, the sample must be in the liquid state above this temperature This behaviour is illustrated more clearly in the curve for *cis*-$[Co(NH_3)_2]Br_2$ Very sharp pronounced peaks were obtained above 260° due to the decomposition of the fused $[Co(NH_3)]Br_2$ On mixing the diammine with an equivalent amount of aluminium oxide, curve *C* was obtained which had a broad endothermic peak at 295° instead of the series of small peaks Apparently, the aluminium oxide aids in the dissociation of the monoammine by forming a larger surface area

The curve for the monoammine, curve *D* showed that the compound fused between 170-210 A capillary tube melting point determination of this compound gave a melting point of 201 203°, which is much lower than the 260° previously reported $^{(3)}$ Again the erratic behaviour of the curve was due to the decomposition of the fused monoammine The peak at 455° must also be related to the dissociation of this compound although the peak temperature was much higher than that found in the other curves The decomposition of the fused monoammine gave a series of small sharp peaks in the GE curves of these compounds also as shown in Fig 5

The DTA curves of the $[Co(NH_3)_n]I_2$ complexes, as given in Fig 4, were also similar to those obtained for the $[Co(NH_3)_n]Cl_2$ complexes The complex, $[Co(NH_3)_6]I_2$, gave DTA curve peak temperatures of 178°, 210° and about 300°, respectively On the basis of the curves for *cis*- and *trans*-$[Co(NH_3)_2]I_2$, the assignment for these peaks is as follows

(a) 178° endothermic peak

$$[Co(NH_3)_6]I_2 \rightarrow [Co(NH_3)_2]I_2 + 4NH_3$$

(b) 210° endothermic peak

$$[Co(NH_3)_2]I_2(s) \rightarrow [Co(NH_3)_2]I_2(l)$$

(c) 300° endothermic peak

$$[Co(NH_3)_2]I_2 \rightarrow CoI_2 + 2NH_3$$

The two compounds, *cis*- and *trans*-$[Co(NH_3)_2]I_2$ gave practically identical DTA curves

The DTA curve for $[Co(NH_3)_6]SO_4$ as shown in Fig 4, *D*, gave two rather broad endothermic peaks with peak temperatures of about 130° and 240°, respectively. It was not possible to assign definite chemical reactions to these peaks.

The DTA curve for $[Co(NH_3)_6](NO_3)_2$, as shown in Fig. 4, *E*, gave two endothermic peaks, with peak temperatures of 137° and 180°, respectively, and an exothermic peak at 210°. The 137° peak is due to the reaction

$$[Co(NH_3)_6](NO_3)_2 \rightarrow [Co(NH_3)_4](NO_3)_2 + 2NH_3$$

while the 180° peak is apparently due to a phase transition since a GE peak, Fig. 6, was not observed in this temperature region. It is obvious that the 210° exothermic peak was due to the explosive decomposition of the tetrammine complex.

Dissociation of $[Co(NH_3)_6(NO_3)_2$. The stoichiometry of the thermal dissociation of $[Co(NH_3)_6](NO_3)_2$ was of interest because of previous studies on the analogous Co(III) compound, $[Co(NH_3)_6](NO_3)_3$. Mass spectrometric analysis studies on the decomposition gases revealed the presence of N_2O, NH_3, NO, N_2, and H_2O. From the gas absorption train and the modified Dumas nitrogen apparatus, the following stoichiometry data were obtained: NH_3/Co, 3.17 found, 3.33 theor.; H_2O/Co, 3.87 found, 4.00 theor.; NH_3/N_2, 1.8 found, 1.77 theor.

Although not all of the reaction products were determined in the analyses, the data suggest that the thermal dissociation reaction is as follows:

$$9[Co(NH_3)_6](NO_3)_2 \rightarrow 3Co_3O_4 + 30NH_3 + 36H_2O + 17N_2 + 4NO + 2N_2O$$

In the thermal dissociation of $[Co(NH_3)_6](NO_3)_3$, ammonium nitrate was also found in the reaction products but nitrogen (II) oxide was absent. For the corresponding nitro-complex $[Co(NH_3)_3(NO_2)_3]$, only nitrogen, water, and Co_3O_4 were obtained.(13)

Acknowledgement.—This work was supported by the U.S. Air Force, Office of Scientific Research, through Grant No. AF-AFOSR-23-63.

(13) G. L. CLARK, A. J. QUICK and W. D. HARKINS, *J. Amer. Chem. Soc.* **42**, 2483 (1920).

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 995 to 998. Pergamon Press Ltd. Printed in Northern Ireland

COMPLEXES OF TETRAPEROXYDITUNGSTATE IONS WITH MANDELIC AND GLYCOLLIC ACIDS

D. H. BROWN
Chemistry Department, Royal College of Science and Technology, Glasgow

(*Received* 27 *November* 1962, *in revised form* 6 *March* 1963)

Abstract—Mandelic and glycollic acids form 2:1 complexes with tetraperoxyditungstate ions over a limited range of pH. The nature of the complex ions formed has been investigated by polarimetric, potentiometric and spectrometric methods.

THE existence of two different peroxytungstate ions was confirmed by JAHR,(1) SOUCHAY(2) and TRIDOT.(3) The two anions WO_8^{2-} and $W_2O_{11}^{2-}$, are formed by the addition of hydrogen peroxide to an aqueous solution of sodium tungstate and adjusting the pH. The reactions involved are

$$WO_4^{2-} + 4H_2O_2 = WO_8^{2-} + 4H_2O$$

$$2WO_8^{2-} + 2H^+ + 3H_2O = W_2O_{11}^{2-} + 4H_2O_2$$

In weak acid solution, where the hexatungstate ion $[HW_6O_{21}]^{5-}$ exists,(4) an excess of hydrogen pyroxide appears to cause the reaction

$$[HW_6O_{21}]^{5-} + 12H_2O_2 = 3[W_2O_{11}]^{2-} + H^+ + 12H_2O$$

The suggested structures(1) for these complex ions involve the O_2^{2-} ions in place of the O^{2-} ions in the normal tungstate ions. Complexes of normal tungstate and of both the peroxytungstate ions with D-tartaric acid have been described.(5,6) The stoicheiometry of these complexes was 1:1 tartaric acid to tungstate, 1:1 tartaric acid to tetraperoxyditungstate and 1:1 tartaric acid to tetraperoxytungstate ions. Since mandelic and glycollic acids also complex with normal tungstate ions,(7) giving 2:1 complexes, they have now been investigated as possible ligands for the peroxytungstate ions.

EXPERIMENTAL AND RESULTS

Fig. 1 shows the potentiometric titration (*a*) of 50 ml of a solution 0.04 M in sodium tungstate, 0.08 M in mandelic acid and 0.5 M in hydrogen peroxide, with 0.1 M sodium hydroxide, using a glass electrode-calomel electrode system. Curve (*b*) shows the results obtained using the above solutions but with the concentration of mandelic acid halved. Curve (*c*) is similar to that described(7) for mandelatotungstate solution and curve (*d*) to that obtained by BIEHLER(8) corresponding to the formation of the $W_2O_{11}^{2-}$ and WO_8^{2-} ions as the pH rises.

The addition of a solution of sodium tetraperoxyditungstate to a solution of L-mandelic acid produces an increase in optical rotation. Using solutions which were

---

(1) K. F. JAHR, *Z. angew. Chem.* **55**, 94 (1941).

(2) P. SOUCHAY, *Bull. Soc. chim. France*, 122 (1942).

(3) G. TRIDOT, *Ann. Chim. (France)*, **10**, 255 (1955).

(4) G. JANDER, *Z. Anorg. Chem.*, **187**, 60 (1930).

(5) M. J. BAILLIE and D. H. BROWN, *J. Chem. Soc.* 3691 (1961).

(6) D. H. BROWN and D. FORSYTH, *J. Chem. Soc.* 1837 (1962).

(7) D. H. BROWN, *J. Chem. Soc.* 4732 (1961).

(8) G. BIEHLER, *Ann. Chim. (France)* **2**, 489 (1947).

J. Inorg. Nucl. Chem. 1963. Vol. 25, pp. 995 to 998. Pergamon Press Ltd. Printed in Northern Ireland

COMPLEXES OF TETRAPEROXYDITUNGSTATE IONS WITH MANDELIC AND GLYCOLLIC ACIDS

D. H. Brown
Chemistry Department, Royal College of Science and Technology, Glasgow

(*Received* 27 *November* 1962, *in revised form* 6 *March* 1963)

Abstract—Mandelic and glycollic acids form 2:1 complexes with tetraperoxyditungstate ions over a limited range of pH. The nature of the complex ions formed has been investigated by polarimetric, potentiometric and spectrometric methods.

The existence of two different peroxytungstate ions was confirmed by Jahr,(1) Souchay(2) and Tridot.(3) The two anions WO_8^{2-} and $W_2O_{11}^{2-}$, are formed by the addition of hydrogen peroxide to an aqueous solution of sodium tungstate and adjusting the pH. The reactions involved are:

$$WO_4^{2-} + 4H_2O_2 = WO_8^{2-} + 4H_2O$$

$$2WO_8^{2-} + 2H^+ + 3H_2O = W_2O_{11}^{2-} + 4H_2O_2$$

In weak acid solution, where the hexatungstate ion $[HW_6O_{21}]^{5-}$ exists,(4) an excess of hydrogen pyroxide appears to cause the reaction

$$[HW_6O_{21}]^{5-} + 12H_2O_2 = 3[W_2O_{11}]^{2-} + H^+ + 12H_2O$$

The suggested structures(1) for these complex ions involve the O_2^{2-} ions in place of the O^{2-} ions in the normal tungstate ions. Complexes of normal tungstate and of both the peroxytungstate ions with D-tartaric acid have been described.(5,6) The stoicheiometry of these complexes was 1:1 tartaric acid to tungstate, 1:1 tartaric acid to tetraperoxyditungstate and 1:1 tartaric acid to tetraperoxytungstate ions. Since mandelic and glycollic acids also complex with normal tungstate ions,(7) giving 2:1 complexes, they have now been investigated as possible ligands for the peroxytungstate ions.

EXPERIMENTAL AND RESULTS

Fig. 1 shows the potentiometric titration (*a*) of 50 ml of a solution 0.04 M in sodium tungstate, 0.08 M in mandelic acid and 0.5 M in hydrogen peroxide, with 0.1 M sodium hydroxide, using a glass electrode-calomel electrode system. Curve (*b*) shows the results obtained using the above solutions but with the concentration of mandelic acid halved. Curve (*c*) is similar to that described(7) for mandelatotungstate solution and curve (*d*) to that obtained by Biehler(8) corresponding to the formation of the $W_2O_{11}^{2-}$ and WO_8^{2-} ions as the pH rises.

The addition of a solution of sodium tetraperoxyditungstate to a solution of L-mandelic acid produces an increase in optical rotation. Using solutions which were

---

(1) K. F. Jahr, *Z. angew. Chem.* **55**, 94 (1941).
(2) P. Souchay, *Bull. Soc. chim. France*, 122 (1942).
(3) G. Tridot, *Ann. Chim.* (*France*) **10**, 255 (1955).
(4) G. Jander, *Z. Anorg. Chem.*, **187**, 60 (1930).
(5) M. J. Baillie and D. H. Brown, *J. Chem. Soc.* 3691 (1961).
(6) D. H. Brown and D. Forsyth, *J. Chem. Soc.* 1837 (1962).
(7) D. H. Brown, *J. Chem. Soc.* 4732 (1961).
(8) G. Biehler, *Ann. Chim.* (*France*), **2**, 489 (1947).

0 04 M in L-mandelic acid, 0 04 M in sodium tungstate and 0 5 M in hydrogen peroxide, the variation in optical rotation (20 cm tube, sodium D light) with pH was measured Each solution was left for 2 hr to reach equilibrium The results are shown in Fig 2 Also shown for comparison are the corresponding graphs of the change in optical rotation with pH of L-mandelic and L-mandelatotungstic acids

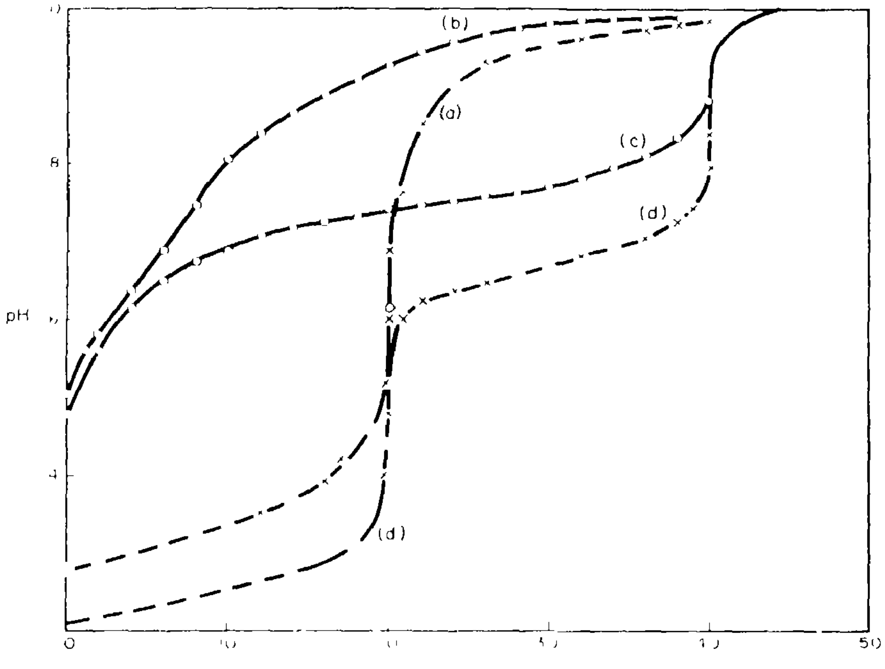


Fig 1 —Potentiometric titrations of 50 ml of solutions (*a*) 0 04 M in sodium tungstate 0 08 M in mandelic acid and 0 5 M in hydrogen peroxide, (*b*) 0 04 M in sodium tungstate and mandelic acid and 0 5 M in hydrogen peroxide, (*c*) 0 04 M in mandelatotungstate, and (*d*) 0 04 M in peroxytungstate, with 0 1 N sodium hydroxide

Ultra-violet spectra of solutions (2×10^{-3} M) of peroxytungstates and mandelatoperoxytungstates were taken at different pHs using comparable hydrogen peroxide solutions as blanks The ion $W_2O_{11}^{2-}$ absorbs at 287 mμ and the WO_8^{2-} ion at 330 mμ The results show that the presence of L-mandelic acid prevents the formation of the WO_8^{2-} ion until the pH of the solution is over eight This change normally occurs about pH 6 5 Similar results were obtained with glycollic acid

Equimolar solutions (0 06 M) of tetraperoxyditungstate and L-mandelic acid were mixed in various proportions and the pH of the solution measured The results are shown in Fig 3, as a graph of pH against mole fraction of mandelic acid Similar results were obtained with glycollic acid The optical rotations of the above solutions were also measured and the results also recorded in Fig 3

DISCUSSION

In Fig 1, neither curves (*a*) nor (*b*) resemble (*c*) corresponding to the formation and decomposition of mandelatotungstate Similarly, curve (*d*) corresponding to the formation of the $W_2O_{11}^{2-}$ and WO_8^{2-} ions is altered by the addition of glycollic

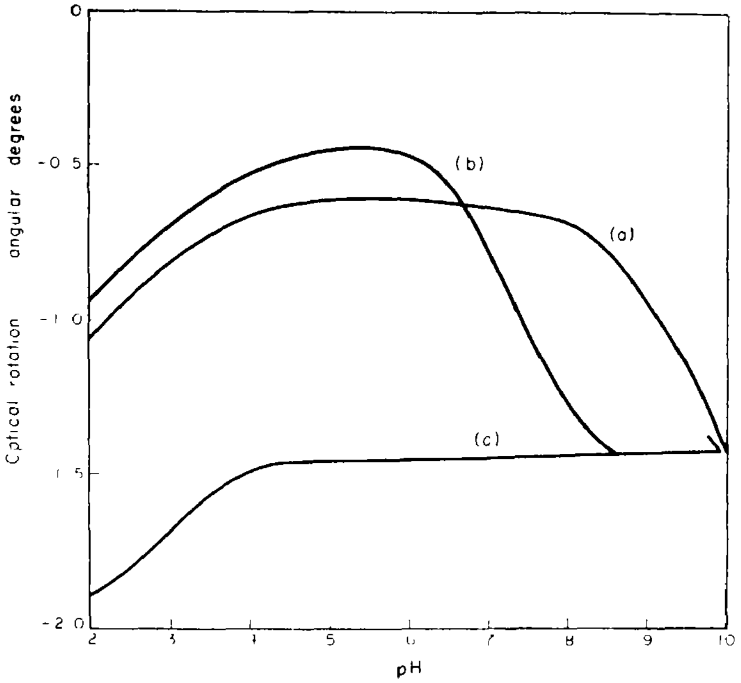


FIG 2 —Plots of optical rotation against pH for (*a*) 0 02 M-(−)-mandelatoperoxytungstate, (*b*) 0 02 M-(−)-mandelatotungstate, and (*c*) 0 02 M-(−)-mandelic acid

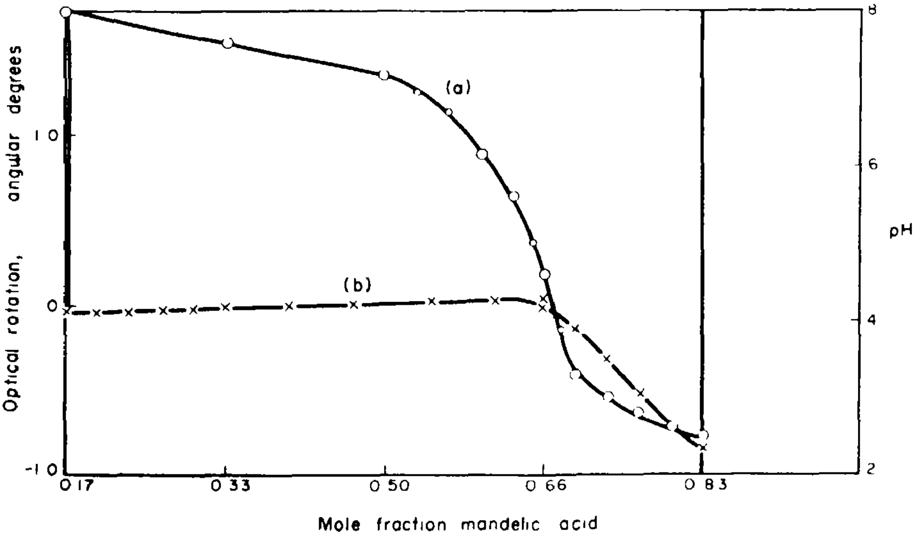


FIG 3 - Plots of (*a*) pH and (*b*) optical rotation against mole fraction of mandelic acid using solutions which were 0 06 M in tetraperoxyditungstate and L-mandelic acid

or mandellic acids—the region of constant pH around pH7 given by $W_2O_{11}^{2-} + 2OH^- + 4H_2O = 2WO_8^{2-} + 5H_2O$, being eliminated Thus the comparison of the graphs in Fig 1, suggests that some form of complex formation has taken place between the peroxytungstate ion or ions and mandelic acid and that either, from (*a*), the complex titrates as a monobasic acid or that only half of the mandelic acid is complexed Curve (*b*) tends to support the latter theory

The ultra-violet spectra show that the tetraperoxyditungstate ions are the predominant species present from pH2 to over pH8 in the presence of mandelic acid and from pH2 to about pH7 in its absence Thus mandelic acid must complex with the tetraperoxyditungstate ions and this complex must be more stable to hydroxyl ion than is the tetraperoxyditungstate ion itself This evidence agrees with the results shown in Fig 2 The enhanced optical rotation shown in curve (a) indicates complex formation of L-mandelic acid Curves (*a*) and (*b*) are similar in shape except that curve (*a*) indicates the formation of a stable complex up to a slightly higher pH viz pH 9 Thus from the ultraviolet spectra and the optical rotation results, L-mandelic acid and tetraperoxyditungstate ions are both complexed to around pH9

Figure 3(*a*) shows the most rapid change of pH when the ratio of mandelic acid to tetraperoxyditungstate ions is 2 1 Figure 3(*b*) confirms the stoicheiometry of the complex as 2 1 mandelic acid to tetraperoxyditungstate ion

Mandelic and glycollic acid complexes with normal tungstate ion are most stable before ionization$^{(7)}$ These complexes can exist in pH conditions where the acids are usually ionised This is thought to be because the hydrogen ions are hydrogen bonded to the oxygen ions of the tungstate group The similarity in the optical rotations (Fig 2) of the L-mandelatotungstate and the L-mandelatotetraperoxyditungstate solutions compared with that of L-mandelic acid, suggests that the ligands are the same in each case, viz mandelic acid, and that they are similarly bonded Discussion of the possible structure must, however, be speculative since there is no definite information about the structures of the peroxytungstates themselves However, there appears to be a marked similarity both in change in optical rotation and in pH range of stability between tungstate complexes and peroxytungstate complexes e g with tartaric acid and mandelic acid The presence of the extra chelating sites in tartaric acid seems to give a complex which is stable over a wider range of pH in both cases

J Inorg Nucl Chem 1963 Vol 25 pp 999 to 1004 Pergamon Press Ltd Printed in Northern Ireland

AZIDE COMPLEXES OF PALLADIUM(II) IN SOLUTION

F G Sherif and K F Michail
Department of Chemistry, Faculty of Science, University of Alexandria, Egypt, U A R

(*Received* 16 *October* 1962, *in final revised form* 10 *February* 1963)

Abstract—Palladium(II) ions give an immediate red-brown colouration with azide ions in solution The system is stable for at least 10 hr and shows no absorption maximum in aqueous solutions In water–acetone mixtures maxima exist between 430–480 mμ, the positions of which depend upon the concentrations of both acetone and azide Spectrophotometric studies indicate the presence of a 1 Pd^{2+} 2 N_3^- complex, with K in = 6 03 ± 1 2 × 10^{-10} for $[Pd(N_3)_2Cl_2]^{-2}$ and the possible formation of 1 1- and 1 4-Pd^{2+} to N_3 complexes in aqueous solutions In water–acetone mixtures the presence of a $Pd(N_3)_4$ complex is indicated Conductimetric titrations confirmed the existence of the diazido and tetrazido forms, and the nature of the charge on the latter was proved by migration experiments

Investigations on the use of the azide ion as a ligand for heavy metallic ions have been extended to the palladium(II) ion Previous work showed that sodium azide reacts with Fe^{3+},(1) Cu^{2+},(2) Cr^{3+},(3) Co^{2+}(4) and UO_2^{2+}(5) ions, giving blood red, brown, green, blue and orange-yellow solutions respectively, and these colours were found to be useful in the analytical determinations of these ions Palladium(II) chloride solution gives a brown-red colour with the azide In the present work, the absorption properties and characteristics of the possible complex ions formed in aqueous and water-acetone mixtures are studied

EXPERIMENTAL

Dried palladium chloride was dissolved in the least amount of standard hydrochloric acid, and then diluted to the desired strength with distilled water The palladium content was determined gravimetrically by precipitation as the dimethyglyoxime complex from acid solution In this way a stock solution containing 0 1 M Pd(II) and 0 16 N HCl was prepared A stock solution of 0 1 M sodium azide was prepared and analysed volumetrically against standard silver nitrate solution using potassium chromate as an indicator A Unicam spectrophotometer S P 500 was used, with a blank solution containing the same concentration of palladium as the test solution Conductivity measurements were carried out using a conductimeter equipped with a magic eye indicator Other procedures have been described previously (3,5)

Monoazido dipyridino–palladium(II)monochloride was prepared in aqueous solution by adding two equivalents of 0 1 M pyridine solution to 50 ml containing 0 05 mole $PdCl_2$ and fourfold excess of NaN_3 Long microscopic orange crystals resembling the branch of a tree were formed The product was further recrystallized from hot water, with a yield of 76 per cent, and decomposed at 262–264°C Their crystal form differed from that of the light yellow pointed crystals of the dipyridino-palladium(II)dichloride(6) obtained from palladium chloride and pyridine Found C, 35 57, H, 2 98, Cl, 10 10 Calc for $[Pd(N_3)py_2]Cl$ C, 35 08 H 2 95, Cl, 10 36%)

---

(1) H K El-Shamy and F G Sherif, *Egypt J Chem* **1,** 35, 257 (1958), **2,** 217 (1959)

(2) G Saini and G Ostocali, *J Inorg Nucl Chem* **8,** 346 (1959)

(3) F G Sherif and W M Oraby, *J Inorg Nucl Chem* **17,** 152 (1961)

(4) P Senise, *J Amer Chem Soc* **81,** 4196 (1959)

(5) F G Sherif and A M Awad, *J Inorg Nucl Chem* **19,** 94 (1961), *Analyt Chim Acta,* **26,** 235 (1962)

(6) H D K Drew *et al*, *J Chem Soc* 1895 (1932)

RESULTS

General absorption properties

Sodium azide reacts instantly with palladium(II) giving a brown-red solution which is stable for ten hours in solutions 0 001 M Pd The stability increased in more concentrated solutions of palladium and on addition of excess azide, but decreased in dilute solutions containing a deficiency of azide In the latter case a gelatinous dark brown precipitate appeared after 2 hr mixing The stability was also increased significantly in the presence of 60–80 per cent acetone

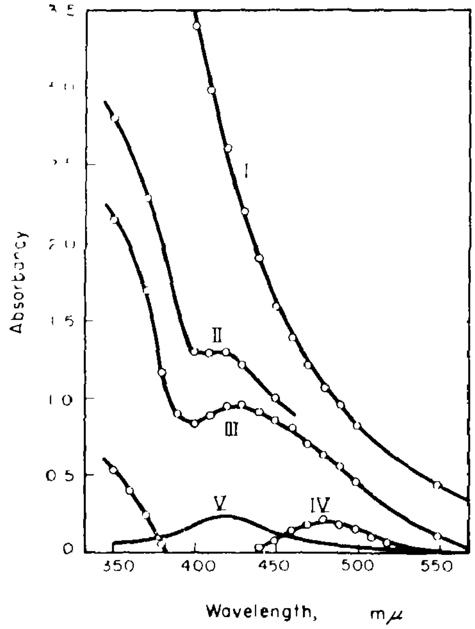


Fig 1 —Absorption curves of palladium(II) azide solutions, 0 001 M Pd^{2+} and 0 004 M N_3^- in water (I) in 60 per cent acetone (II), in 80 per cent acetone (III), 0 001 M Pd^{2+} and 0 001 M N_3^- in 80 per cent acetone (IV), 0 001 M Pd^{2+} in water using water as a blank (V)

No maximum was detected in the absorption curve of the palladium azide in aqueous solutions in the visible region of the spectrum, and the absorbancy decreased sharply between 350 and 600 mμ The intensity was increased by gradually increasing the azide concentration until the ratio of palladium to azide reached about 1 4 Immiscible solvents such as benzene, carbon tetrachloride and ethyl acetate do not extract the colour, but acetone gradually decreases the intensity as its concentration in the solution is increased Meanwhile, a shoulder appears at 430 mμ on the absorption curve of the 50 per cent water–acetone solution and grows to a well-defined maximum at 80 per cent v/v acetone At this acetone concentration the position of the maximum shifts to longer wavelengths on gradually decreasing the azide concentration In a 0 001 M solution containing equimolar Pd^{2+} and N_3^- and 80 per cent v/v acetone, the maximum absorption occurs at 480 mμ Representative curves are shown in Fig 1 The absorbancy index of an aqueous solution containing excess azide was found to be 2200 at 430 mμ compared to 950 at the same wavelength and in 80 per cent v/v acetone

Structure of the palladium azide complexes

The usual spectrophotometric methods for the investigation of structural relations in coloured solutions were applied, viz. Job's continuous variation method, the molar ratio and the slope ratio methods. Conductimetric titrations and qualitative migration experiments were also carried out. Several Job plots were made from 350 to 500 mμ at 10 mμ intervals, and at total concentrations 0.0002, 0.0005, 0.002, 0.01 and 0.02 M, in both water and in water-acetone mixtures. In this way the changes in the positions and intensities of the maxima reflect the type of the complex formed.(7) Typical curves are given in Fig. 2. In aqueous solutions the 1:2 compound appears to be the

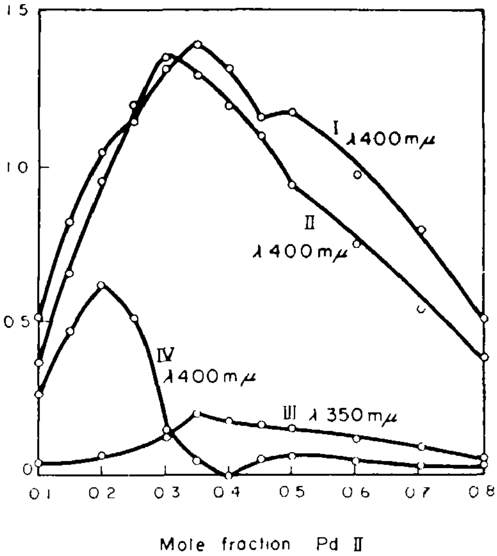


FIG. 2.—Continuous variation method. In aqueous solutions: total concentrations 0.002 M (I), 0.02 M and 0.1 cm cell (II), 0.0002 M (III). In 80% acetone, total concentration 0.0002 M (IV).

predominant species at all dilutions, 1:1 complex probably being formed in dilute solutions, as indicated by the shoulder in curve I, this shoulder is more definite at shorter wavelengths. However, after one week this shoulder disappeared, the corresponding species PdN_3^+ is probably unstable, while the 1:2 complex persisted. Another weak unstable shoulder appeared at 1:4 molar ratio which increased in intensity and changed slightly to a broad maximum on approaching longer wavelengths at 500 mμ. In 80 per cent v/v acetone there is a sharp and stable maximum at 1:4 molar ratio, corresponding to $Pd(N_3)_4^{2-}$, at all wavelengths. In acetone there is also another weak but stable maximum at about 0.5 mole fraction palladium.

Although there were probably at least three complexes present in aqueous solutions, the 1:2 species appeared to be the most stable. The molar ratio method was applied to several concentrations of Pd^{2+}, viz. 0.001, 0.0008 and 0.0004 M with a ratio of $Cl^-:Pd^{2+} = 3.6:1$. Increasing amounts of 0.1 M sodium azide were added to every solution of each run and the solution diluted with water to constant volume and the absorption of each solution was recorded at different wavelengths. In every case the curve of absorbancy versus equivalents of azide rises sharply from the origin and then becomes almost horizontal when two equivalents of azide have been added, confirming the existence of the 1 : 2 complex as the main coloured component of the system. Other breaks indicate the formation of the 1 : 4 species. Since Pd(II) forms complexes with chloride ion,(8) we assume the existence of $PdCl_4^{2-}$ in solutions with $Pd^{2+} : Cl^- = 1 : 4$. An approximate equilibrium constant for the reaction

---

(7) F. G. SHERIF and A. M. AWAD, *J. Inorg. Nucl. Chem.* **24**, 179 (1962).

$$[PdCl_4]^{2-} + 2N_3^- \rightleftharpoons [Pd(N_3)_2Cl_2]^{2-} + 2Cl^- \qquad (1)$$

was determined by applying the molar ratio method, Fig. 3, to solutions containing 0.0004 M Pd(II) in which the Cl⁻ concentration was adjusted to 0.0016 N, with increasing amounts of sodium azide. The ionic strength was kept constant at 0.0044 by

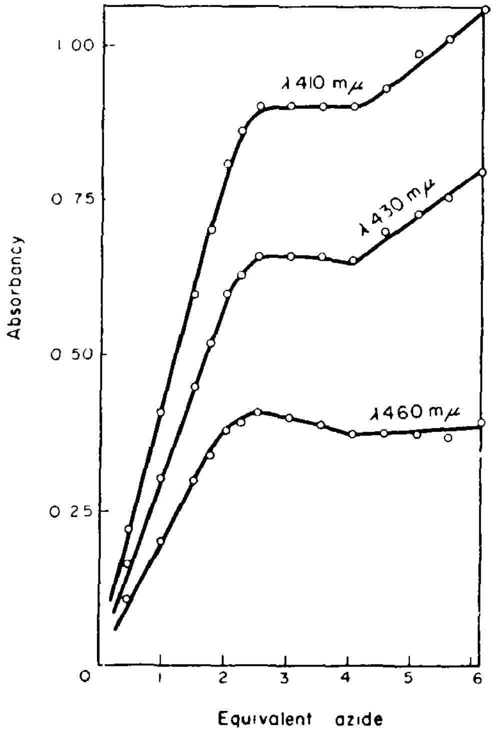


FIG. 3.—Molar ratio method. Concentration of Pd^{2+} = 0.0004 M.

adding the appropriate amounts of sodium perchlorate. If Beer's law applies, the concentration of the 1 : 2 compound will be proportional to the absorption at a fixed wavelength. It is also assumed that the reaction is complete when the absorbancy reaches its maximum value E_m after the addition of a slight excess of the azide. If the adsorption at the stoicheiometric ratio of 1 : 2 is E_s, then

$$\alpha = \frac{E_m - E_s}{E_m} \quad \text{and} \quad K_{in} = \frac{(\alpha C)(2\alpha C)^2}{C(1-\alpha)}$$

---

(8) A. K. SUNDARAM and E. B. SANDELL, *J. Amer. Chem. Soc.* **77**, 855 (1955); G. I. AYRES, *Analyt. Chem.* **25**, 1623 (1953).

where C is the concentration of Pd(II) equivalent to the total concentration of the complex$^{(9)}$ The mean value K_{in} for reaction (1), at different wavelengths, was found to be $6\ 03 \pm 1\ 2 \times 10^{-10}$

The existence of the 1 2 form was further confirmed by applying the slope ratio method at arbitrarily selected wavelengths In each of two series of solutions, one of the reagents was maintained in a constant excess at 0 0005 M, and the other varied from 0 00005 to 0 0003 M, with the results shown in Fig 4, the ratio of the slopes of lines I and II was 1 2 A slight deviation from this value was found at higher

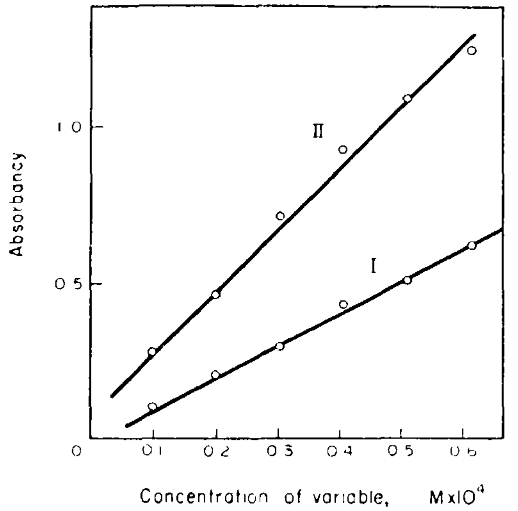


Fig. 4 — Slope ratio method at 350 mμ (I) palladium(II) constant, (II) azide constant, both at 0 0005 M

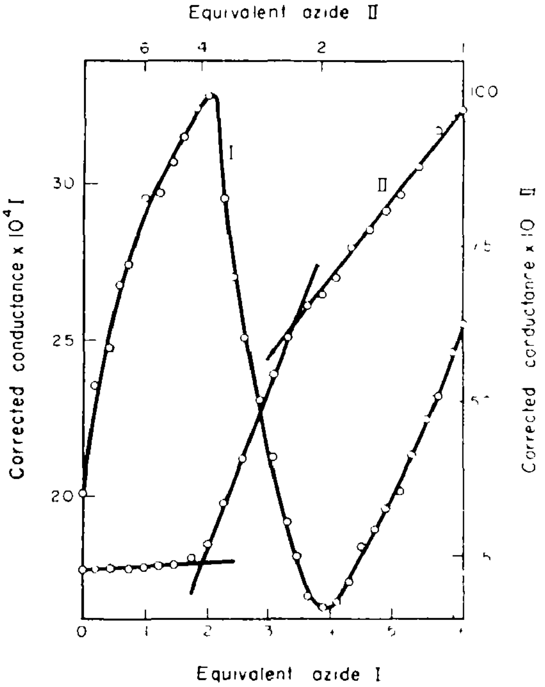


Fig 5 Conductimetric titrations (I) Sodium azide added to palladium(II) (II) Palladium(II) added to sodium azide

wavelengths e g 1 2 2 at 500 mμ, which might be due to the contribution of the 1 4 form Such a value would permit the existence of the 1 4 form to the extent of one tenth that of the 1 2 one at this particular dilution

---

(9) A E Harvey and D L Manning, *J Amer Chem Soc* **72**, 4488 (1950)

Conductimetric titrations were carried out at room temperature between solutions of 0 1 M sodium azide and 0 0016 M Pd(II) containing 0 008 N HCl, in a 100 ml vessel with two platinized platinum electrodes 1 cm^2 in area and 0 3 cm apart Absolute conductivities were not measured, structural evidence being derived from discontinuities in the relative conductance curves, (Fig 5) The same shape of curve was obtained by titrating 0 1 NaN_3 in 60 per cent v/v acetone against a solution containing 0 0014 M Pd^{2} and 0 0022 M HCl in 60 per cent acetone The breaks in curve I indicate the formation of 1 2 and 1 4 species The acid present in the solution apparently did not complicate the shape of the curves, and each hydrazoic acid molecule displaced interacts with palladium ion Reverse titrations entailing the addition of 0 01 M Pd^{2+} solution containing 0 016 N HCl to 30 ml of 0 002 M sodium azide in aqueous solution gave a curve (Fig 5) with two breaks at 1 4 and 1 2 Pd^{2} N_3

The presence of the 1 4 form was confirmed by migration experiments in a tube filled with 1 M sodium chloride solution as a carrier A solution 0 1 M Pd^{2+} containing a large excess of azide and 0 36 N Cl^- introduced carefully at the centre of the tube and a potential gradient of 1 V/cm was applied, after 15 min, a definite migration of the red boundary towards the anode was apparent indicating the presence of the negatively charged ion $Pd(N_3)_4^{2}$

J. Inorg. Nucl. Chem. 1963. Vol. 25, pp. 1005 to 1010. Pergamon Press Ltd. Printed in Northern Ireland

SPECTROPHOTOMETRIC STUDY OF COMPLEXES OF TITANIUM WITH SULPHOSALICYLIC ACID AND EDTA USING AUXILIARY COMPLEXING AGENTS IN THE JOB'S METHOD*

N. Mahadevan, R. M. Sathe and Ch. Venkateswarlu
Analytical Division, Atomic Energy Establishment Trombay, Bombay, India

(*Received* 10 *August* 1962, *in revised form* 2 *February* 1963)

Abstract—Complex formation between Ti(IV) and sulphosalicylic acid was reinvestigated. Job's method of continuous variation in equimolar solutions indicated a complex TiR in 1.85 N sulphuric acid. In the pH range of 3.1–5.0, a complex TiR_2 was found, when malonic acid was used as the auxiliary complexing agent.

The composition of the colourless Ti(IV)–EDTA at pH 5.0 was also shown to be 1:1 using the colour forming SSA as the auxiliary complexing agent.

Log β_2 of Ti–SSA_2 was computed as 23.1 from the reported stability constant of Ti–EDTA.

SULPHOSALICYLIC acid (henceforth referred to as SSA) is well known for its versatile complexing of metal ions. Its complexes with cations like Fe^{3+}, UO_2^{2+}, Cu^{2+} and Be^{2+} have already been investigated.(1–4) The complexes of titanium have been studied by SOMMER(5) using different spectrophotometric methods, which however, did not give concordant results regarding the composition of the complexes. In particular, Job's method in equimolar solutions has not led to satisfactory results.

Job's method of continuous variation in equimolar solutions(6) is very commonly used in spectrophotometric studies of metal complexes. Several papers have appeared pointing out the limitations of this method and suggesting modifications to suit more complicated situations.(7,8,9) The authors have, earlier, suggested the purposeful addition of an auxiliary complexing agent(10) to extend the usefulness of this method to cases where the free metal ion undergoes hydrolysis and polymerization under the conditions of complex formation. In the present paper, the coloured complexes of Ti–SSA and the colourless complex of Ti–EDTA were studied using the above modification, wherever possible.

EXPERIMENTAL

For the titanium solution E. Merck titania was dissolved in hydrofluoric acid and the calculated amount of 1:1 sulphuric acid was added and just fumed to remove the fluoride. It was diluted to give a final solution of 1·85 N acidity SSA and EDTA (disodium salt) were of E Merck grade All other reagents were of BDH AnalaR grade

---

* Presented at the 49th session of the Indian Science Congress held at Cuttack in 1962.

(1) R. T. FOLEY and R. C. ANDERSON, *J. Amer. Chem. Soc.* **70**, 1195 (1948).
(2) R. T. FOLEY and R. C. ANDERSON, *J. Amer. Chem. Soc.* **71**, 909 (1949).
(3) S. E. TURNER and R. C. ANDERSON, *J. Amer. Chem. Soc.* **71**, 912 (1949).
(4) H. V. MEEK and C. V. BANKS, *J. Amer. Chem. Soc.* **73**, 4108 (1951).
(5) L. SOMMER, *Coll. Czech. Chem. Comm.* **22**, 453 (1957).
(6) P. JOB, *Analyt. Chim.* **9**, 113 (1928).
(7) W. C. VOSBURGH and G. R. COOPER, *J. Amer. Chem. Soc.* **63**, 437 (1941).
(8) W. C. VOSBURGH and R. K. GOULD, *J. Amer. Chem. Soc.* **64**, 1630 (1942).
(9) L. SOMMER and M. HNILIČKOVA, *Bull. Soc. Chim. France* 36 (1959).
(10) R. M. SATHE and CH. VENKATESWARLU, *Coll. Czech. Chem. Comm.* **27**, 701 (1962).

All extinction measurements were made on a Beckman spectrophotometer, Model DU, using 1·00 cm silica cells For pH measurements, a Marconi instrument of type 511 D was used

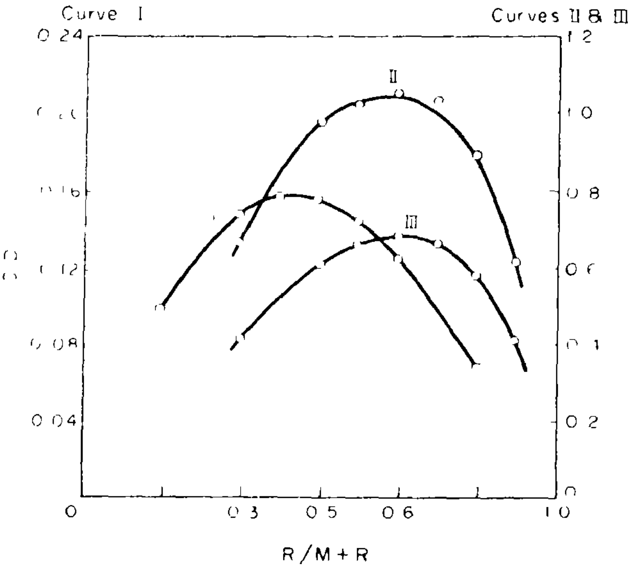


FIG 1 Curve I Job's curve in equimolar solutions for Ti and SSA in 1·85 N sulphuric acid at 400 mμ, ($C_M + C_R$) = 6·25 × 10^{-2} M
Curve II Job's curves in equimolar solutions for Ti and SSA in presence of malonic acid (4·8 × 10^{-2} M) $C_M + C_R$ = 7·5 × 10^{-3} M, pH = 3·1, λ = 380 mμ
Curve III $C_M + C_R$ = 7·5 × 10^{-3} M, pH 3·1, λ 400 mμ

Titanium SSA system

SOMMER[1] has observed that in the spectrum of titanium in the presence of a very large excess of SSA, the extinction at 430 mμ, increases steeply in the pH range 1·0 1·5 and reaches a maximum value at pH 1·9 It then remains constant up to pH 5·0 Above this pH, it decreases again and becomes constant only above pH 10·6 Even in this pH range, the solutions appear clear and the hydrolysed products precipitate only on keeping overnight From the shape of this curve, he has concluded that the first complex is formed below pH 1·0, and is then converted into the second complex by pH 1·9 In the range 1·9–5·0, the second complex predominates Later the second complex adds yet another molecule of the ligand He was, however, unable to confirm the compositions of these complexes in the said pH ranges by using JOB's method in equimolar solutions

During a reinvestigation, the authors found that titanium solutions (~10^{-1} M) give a greenish yellow colour with SSA even in 1·85 N sulphuric acid At this acidity, JOB's method with equimolar solutions indicated the formation of TiR Curve I in Fig 1 gives the experimental data with $C_M + C_R$ = 6·25 × 10^{-2} M at 400 mμ The maximum of the curve is however, slightly shifted to the high metal side

It has been further observed that addition of oxalic acid to a mixture of Ti and SSA resulted in a hyperchromic effect indicating the formation of a mixed complex at this acidity, 1·85 N Similar behaviour is exhibited by titanium in a number of systems such as X-Ti–Oxalic acid, where X is gallic acid, catechol, chromatropic acid, etc , under conditions of acidity, where Ti forms a 1 1 complex with X alone These systems are under further investigation

Regarding the formation of TiR_2, SOMMER found that JOB's method in equimolar solutions did not give satisfactory results Hence, the authors felt that their method should give better results The validity of the modification is demonstrated in the following derivation

Let $M + nA \rightleftharpoons MA_n$, so that $K = [MA_n]/[M][A]^n$

and $M + qB \rightleftharpoons MB_q$, so that $K^1 = [MB_q]/[M][B]^q$,

where A is the reagent under consideration and B the auxiliary complexing agent. When B is in large constant excess, [B] can be taken as constant throughout the continuous variation experiment

so that $K^1[B]^q = [MB_q]/[M]$

or $L[M] = [MB_q]$,

where $L = K^1[B]^q$

When x volumes of reagent and $(1 - x)$ volumes of metal, both of the same molarity m, are mixed and C_1, C_2 and C_3 are the final equilibrium concentrations of the free metal M, free reagent A and the complex MA_n respectively, it can be shown that $n = x_{max}/(1 - x_{max})$⁽⁸⁾ which is the same as in the absence of the auxiliary reagent B.

Oxalic acid was tried as the auxiliary complexing agent to determine the composition of TiR_2. The Ti SSA complex was completely destroyed. The obvious choice was, therefore, malonic acid, which can be expected to form weaker complexes than oxalic acid. In the presence of a constant excess of malonic acid (4.8×10^{-2} M), JOB's method in equimolar solutions was carried out at pH 3.1, maintaining constant ionic strength. The maxima in the curves II and III (Fig. 1) indicate that TiR_2 exists in this pH region. A similar experiment was carried out at pH 5.0. Since the resultant colour intensity was feeble, extinction measurements were made with 5.00 cm cells. The curve flattened but the maximum occurred near 1:2 indicating the existence of the same complex.

The solutions containing Ti and SSA in the high pH region are practically colourless. From the spectra of solutions containing a large excess of SSA and small but constant amount of metal at pHs of 5.0, 5.5 and 5.8, it has been observed that there is a shift of the absorption maximum towards lower wavelengths, accompanied by a decrease in extinction in the entire spectral range studied as the pH increases. This indicates the formation of another species. Experiments were carried out to see if this new species can bleach the colour of Ti-protocatechuic acid (PCA) at pH 8.0. With 2.5×10^{-5} M Ti, a thirty fold excess of SSA over PCA did not show any bleaching whatsoever. This indicated that this colourless complex is too weak to be studied by the method given below.

Titanium-EDTA *system*

In this case, equimolar solutions of titanium and disodium salt of EDTA, were varied continuously at pH 5.0 in the presence of a large constant excess of SSA as the auxiliary complexing agent. Curve II in Fig. 2 shows the extinction values of these solutions at 400 mμ while curve I those of the corresponding solutions in the absence of EDTA. The differences of the extinction values of the two solutions were plotted as curve III. These differences are a measure of the concentration of titanium–EDTA. The maximum in the curve indicates a composition of 1:1 for this system. Curve IIIa in Fig. 2 is a plot of similar differences at 380 mμ.

In view of the mixed complex formation reported earlier,⁽¹¹⁾ tests were conducted in this system. This was done by adding increasing amount of EDTA to a solution containing titanium and a large excess of SSA. The continuous decrease in the extinction value with increase in EDTA indicates progressive convertion of Ti-SSA_2 to Ti–EDTA. The entire spectrum from 340 to 450 mμ was recorded for the Ti–SSA_2 complex in the presence and absence of EDTA (Fig. 3). Since the spectra are very much the same, it is concluded that there is no mixed complex in this case.

Calculation of stability constant of Ti–$(SSA)_2$

Since it is found that titanium forms a 1:1 complex with EDTA and a 1:2 complex with SSA and no mixed complex is formed when both ligands are present, the following equilibria can be written. Free titanium does not exist as Ti^{4+} in solution which are not very acidic, and it is therefore,

---

(11) V. T. ATHAVALE, V. P. MADHAVAMENON and CH. VENKATESWARLU, *Analyst* 85, 208 (1960).

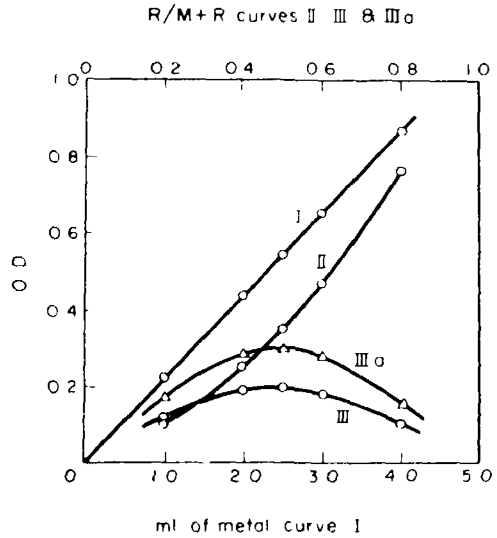


Fig. 2 — Job's curves in equimolar solutions for the titanium–EDTA complex
$C_M + C_R = 1.25 \times 10^{-4}$ M, $C_{SSA} = 3.94 \times 10^{-2}$ M
Curve I Ti–SSA, at 400 mμ
Curve II Ti–SSA EDTA, at 400 mμ
Curve III Difference of curves I and II at 400 mμ
Curve IIIa Similar difference at 380 mμ

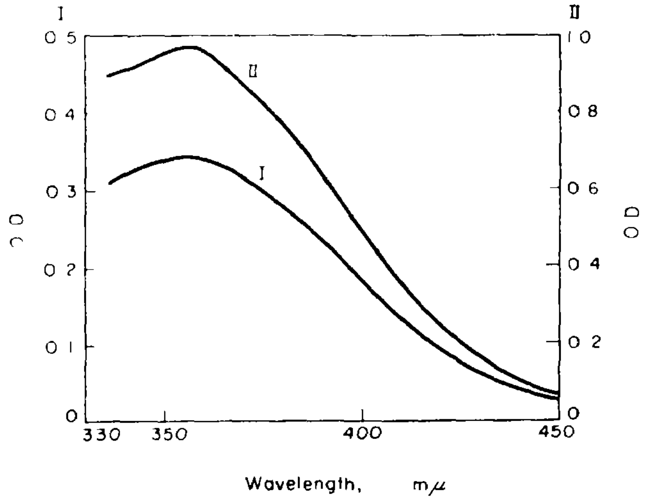
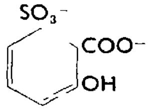


Fig 3 — Absorption spectra of titanium–SSA in presence (curve I) and absence (curve II) of EDTA
$C_M = 6.25 \times 10^{-5}$ M, $C_{SSA} = 3.94 \times 10^{-2}$ M
$C_{EDTA} = 1.87 \times 10^{-4}$ M

represented as the titanyl ion TiO^{2+} (12) SSA is represented as HA where HA is



and EDTA is shown as H_2Y where Y^{4-} is the anion of EDTA

$$TiO^{2+} + 2HA \rightleftharpoons TiOA_2 + 2H^+$$

$$k_1 = [TiOA_2][H^+]^2/[TiO^{+2}][HA]^2 \tag{1}$$

$$TiO^{2+} + H_2Y \rightleftharpoons TiOY + 2H^+$$

$$k_2 = [TiOY][H^+]^2/[TiO^{+2}][H_2Y] \tag{2}$$

$$TiOA_2 + H_2Y \rightleftharpoons TiOY + 2HA$$

$$k_3 = [TiOY][HA]^2/[TiOA_2][H_2Y] \tag{3}$$

$$TiO^{2+} + Y^{4-} \rightleftharpoons TiOY$$

$$k_4 = [TiOY]/[TiO^{+2}][Y^{-4}] \tag{4}$$

$$H_2Y \rightleftharpoons 2H^+ + Y^{4-}$$

$$k_5 = [Y^{4-}][H^+]^2/[H_2Y] \tag{5}$$

Now, it can be shown that

$$k_3 = k_2/k_1 \tag{6}$$

$$k_5 = K_3K_4 \tag{7}$$

where K_3 and K_4 are the third and fourth dissociation constants of EDTA

$$k_2 = k_4k_5 \tag{8}$$

k_3 is computed from the data given in Fig 2 $TiOA_2$ was calculated from the observed optical density with the help of a calibration curve for titanium in the presence of excess SSA

$$[TiOY] = [TiO^{2+}{}_{total}] - [TiOA_2]$$

$$[HA] = [HA_{total}] - 2\,[TiOA_2]$$

$$[H_2Y] = [H_2Y_{total}] - [TiOY]$$

log k_3 was then calculated as 1.24 Further a bleaching curve (Fig 4) was obtained by adding increasing amounts of EDTA to a mixture of Ti (6.25×10^{-4} M) and large amount of SSA (0.04 M)

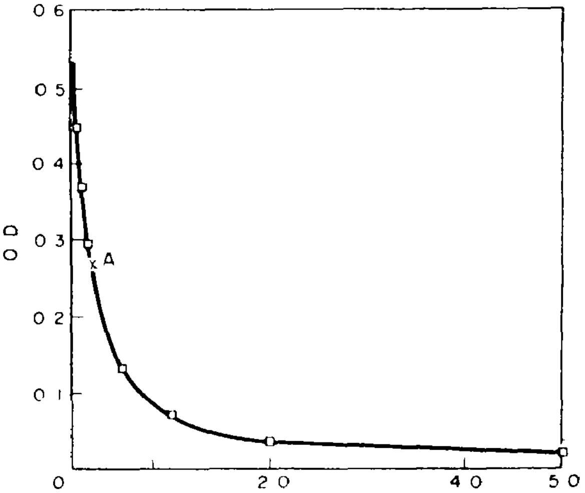


Fig. 4 Bleaching of the colour of Ti-SSA$_2$ complex by EDTA A is the point of half bleaching
$C_{Ti} = 6.25 \times 10^{-4}$ M,
C_{SSA} 3.94×10^{-2} M
C_{EDTA} 2.69×10^{-2} M

---

(12) L. Sommer, *Bull Soc Chim France*, 862 (1959)

The value of k_3 was confirmed from the amount of EDTA at the point A, where the O.D. has fallen to half the original value

$$[TiOA_2] = [TiOY]$$
$$k_3 = [HA]^2/[H_2Y] \qquad (9)$$

so log k_3 = 1.22

The value of log k_4 has been reported by Pecsok and Maverick[13] from a polarographic study as 17.3. From a combination of 6, 7 and 8 log k_1 was calculated as −0.33

$$HA \rightleftharpoons H^+ + A^- \qquad k' = \frac{[H^+][A^-]}{[HA]} \qquad (10)$$

From relations (1) and (10), the pH independent stability constant of Ti SSA$_2$ complex is given by

$$\beta_2 = \frac{k_1}{(k')^2}$$

i.e.,

$$\log \beta_2 = \log k_1 - 2 \log k'$$
$$= -0.33 + 2 \times 11.74 = 23.15$$

DISCUSSION

In the reinvestigation of the Ti–SSA system, the modified Job's method has yielded fruitful results in establishing the existence of TiR$_2$ in the pH region 3.5. The same method has been shown to be successful in arriving at the composition of the colourless complex, Ti–EDTA, using a reagent, forming a coloured complex with titanium as the auxiliary agent. Babko[14] has studied Ti-salicylic acid system using oxalic acid as the auxiliary ligand where $C_{\text{oxalic acid}} \sim \frac{1}{2}(C_M + C_R)$. He arrives at a composition of 1:1 for titanium to salicylic acid, whereas the composition under the same pH conditions by the logarithmic analysis is given as 1:2. Kleiner[15] has also studied the colourless Ti–F complex using hydrogen peroxide as the colour forming auxiliary agent but again not in large excess. Since the amount of the auxiliary complexing agent is small compared to $C_M + C_R$ in both cases mentioned above, the equilibrium concentration of the auxiliary complexing agent will not remain constant during the continuous variation experiment, thus vitiating the validity of the derivation given in this paper. Further work is in progress with the system, that Babko has studied, as well as with other systems using different auxiliary complexing agents.

Acknowledgement—We wish to thank Dr. V. T. Athavale for his keen interest and useful discussions during the progress of this work.

---

(13) R. L. Pecksok and E. F. Maverick, *J. Amer. Chem. Soc.* **76**, 358 (1954).

(14) A. K. Babko, A. I. Volkova and T. E. Getman, *Russ. J. Inorg. Chem.*, Eng. Trans. by Chem. Soc., London, (1961) May, p. 529.

(15) K. E. Kleiner, *J. Gen. Chem. USSR*, 1952, **22**, 17, (1952) English Translation p. 15.

J Inorg Nucl Chem 1963, Vol 25, pp 1011 to 1019 Pergamon Press Ltd Printed in Northern Ireland

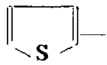
STUDIES ON TTA COMPLEXES WITH METAL IONS—II

INVESTIGATIONS OF SOME TETRAVALENT COMPLEXES IN THE SOLID STATE*

Y Baskin and N S Krishna Prasad†
Metallurgy Division, Argonne National Laboratory, Argonne, Illinois

(*Received* 12 *November* 1962, *in revised form* 4 *February* 1963)

Abstract—Single crystals of TTA chelates of tetravalent uranium, thorium, hafnium, zirconium, cerium and plutonium have been prepared X-ray diffraction data revealed that the compounds are isostructural, with only slight variations in their orthorhombic cell dimensions Studies were also conducted of the optical properties, infrared absorption spectra and differential thermal analysis curves of the compounds

Thenoyltrifluoroacetone (TTA)  —CO—CH$_2$—CO—CF$_3$ forms complexes with various metal ions which can be extracted from aqueous solutions by using nonpolar solvents such as benzene or carbon tetrachloride[1-7] Much of the work reported in the literature pertains to the solvent extraction purifications and analytical applications involving the complexing agent, but little work has been conducted on the nature of the metal–TTA complexes in the solid state In an earlier paper (Part I)[8], uranyl–TTA complex in an aqueous–alcoholic medium was investigated by spectrophotometric and potentiometric methods This paper deals with crystallographic, optical, infra-red spectra and differential thermal anaysis studies of TTA chelates of tetravalent uranium, thorium hafnium, zirconium, cerium and plutonium

EXPERIMENTAL

Preparation of the complexes

UT$_4$ To a solution of tetravalent uranium, obtained by photochemical reduction of uranyl nitrate in 50 per cent alcohol, was added an alcoholic solution of TTA‡ of equivalent strength The amount added was slightly less than that required to complex all of the uranium, thus leaving a slight excess of metal ions in solution The precipitate formed was filtered, washed first with water and then with alcohol (UT$_4$ is far less soluble in alcohol than is UO$_2$T$_2$) The crystals were finally dried and stored in a desiccator at room temperature

---

* Work performed under the auspices of the U S Atomic Energy Commission

† Dr Baskin is an Associate Ceramist, Metallurgy Division, Argonne National Laboratory, Argonne, Illinois At the time the study was conducted, N S Krishna Prasad was a participant in the International Institute of Nuclear Science & Engineering at Argonne National Laboratory He is now at the Chemistry Division, Atomic Energy Establishment, Trombay, India

‡ Thenoyltrifluoroacetone (TTA) manufactured by Columbia Organic Chemical Company, Inc , Columbia, South Carolina

(1) M Calvin and E L Zebroski, U S A E C Report BC-42 (1947)

(2) W M Latimer, U S A E C Report BC-61 (1947)

(3) H A Levy and A Broido, U S A E C Report CNL-37 (1948)

(4) E H Huffman and L J Beaufait, *J Amer Chem Soc* **70**, 3179 (1948)

(5) R A Bolomey and L Wish, U S A E C Report ORNL-136 (1948)

(6) E K Hyde, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955, Vol 7, p 282, United Nations (1956)

(7) F L Culler, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955, Vol 9, pp 468, 471, 473 United Nations (1956)

(8) K M Abubacker and N S Krishna Prasad, *J Inorg Nucl Chem* **16**, 296 (1961)

TABLE 1 – X-RAY POWDER

UT$_4$				ThT$_4$				HfT$_4$			
I/I vis	*d* (obs)	*d* (calc)	*hkl*	*I/I* vis	*d* (obs)	*d* (calc)	*hkl*	*I/I* vis	*d* (obs)	*d* (calc)	*hkl*
5	10 72	10 74	001	2	10 53	10 70	001	10	10 78	10 79	001
10	9 36	9 51	011	10	9 46	9 50	011	40	9 51	9 54	011
100	8 80	8 86	200 120	100	8 84	8 93	200	100	8 67*b*	8 78	120
1	6 86	6 831	121			8 83	120			8 63	200
10	5 72	5 755	031	5	8 34	8 38	111	5	7 31	7 412	021
10	5 37	5 368	002	5	7 38	7 43	021	5	6 81	6 811	121
15	5 12	5 113	320	2	6 46	6 503	211	20	6 39	6 400	211
60	4 60	4 616	321	10	5 70	5 708	221	5	5 70	5 752	031
		4 590	122 202	2	5 36	5 349	002	15	5 44	5 457	131
20	4 45	4 479	212	15	5 14	5 157	040			5 397	002
		4 467	141			5 152	320	20	5 01	5 010	320
		4 428	240	1	4 85	4 854	231	5	4 80	4 786	231
2	4 20	4 188	222	60	4 58	4 589	122	70	4 59	4 598	122
25	4 08	4 093	401			4 588	202			4 576	202
		4 063	420	30	4 46	4 496	141	30	4 42	4 454	141
5	3 88	3 899	312			4 478	212			4 389	240
		3 864	340			4 469	240	15	4 18	4 175	222
1	3 82	3 822	051	1	4 17	4 192	222	50	3 97	3 973	420
20	3 71	3 702	322	40	4 08	4 094	420	20	3 82	3 814	340, 051
2	3 53	3 525	013	5	3 85*b*	3 896	340	30	3 70	3 705	042
5	3 42	3 416	402			3 850	051	2	3 51	3 489	251
		3 415	242	30	3 71	3 713	042	5	3 41	3 406	242
15	3 36	3 347	440 520			3 711	322	30	3 30	3 294	440
2	3 20	3 201	351	10	3 41	3 427	242	15	3 17	3 180	351
		3 196	441	20	3 36	3 376	160	1	3 04	3 035	261
2	2 94	2 932	323			3 373	440	2	2 93	2 940	043
15	2 84	2 840	442			3 372	520			2 922	323
2	2 80	2 792	333	5	3 21	3 231	351	10	2 87	2 858	451
		2 783	403			3 208	260	20	2 79*b*	2 796	522
15	2 58*b**	2 577	433	5	3 05*b*	3 073	261			2 780	601
		2 568	124, 204			3 037	531	10	2 67	2 675	271
10	2 46	2 456	560	5	2 92	2 935	540	20	2 57	2 579	124
		2 450	353			2 915	451			2 576	204
5	2 38	2 376	324	20	2 85	2 857	620			2 560	551, 433
5	2 30	2 307	453			2 842	071	1	2 53	2 526	542
		2 300	334	2	2 77	2 795	333	10	2 42	2 422	560
		2 295	404			2 785	403	5	2 38	2 387	711
15	2 23*b*	2 240	424	1	2 71	2 723	460			2 385	044
		2 233	562			2 707	271			2 375	324
		2 226	154	10	2 58	2 578	080	15	2 28	2 288	453, 404
10	2 09	2 097	354			2 577	640			2 272	642
		2 094	524, 444	10	2 56	2 562	124, 204			2 270	363
		2 086	125, 205	10	2 47	2 476	560	10	2 23	2 233	613
10	2 04	2 037	812			2 462	711			2 231	154
		2 032	1 10 0			2 457	353	15	2 20	2 203	344
		2 031	760, 840	5	2 37	2 374	044 324			2 195	722
				5	2 32	2 321	642			2 190	480
						2 309	453	15	2 09	2 096	354 125
				5	2 29	2 299	334			2 094	205
						2 294	404			2 087	444
				20	2 24	2 253	173			2 082	215
						2 246	722			2 081	524
						2 244	054	2	2 03	2 020	831
				2	2 20	2 205	344				
				10	2 09	2 096	205, 125				
						2 081	444, 524				
				10	2 04	2 049	1 10 0				
						2 048	760, 812				
						2 047	840				

---

* *b* = broad

DIFFRACTION DATA

ZrT$_4$

I/*I* vis	*d* (obs)	*d* (calc)	*hkl*
10	10 55	10 78	001
20	9 44	9 53	011
100	8 69*b*	8 79	120
		8 64	200
2	6 77	6 812	121
5	5 69	5 760	031
2	5 04*b*	5 105	040
		5 015	320
60	4 57	4 595	122
		4 572	202
30	4 45	4 462	212
		4 458	141
20	4 18	4 173	222
50	3 97	3 977	420
15	3 82	3 819	340, 051
15	3 68*b*	3 707	042
		3 672	322
5	3 42	3 407	242
15	3 29	3 291	440
5	3 17	3 185	351
		3 178	033
		3 167	260
1	3 03	3 038	261
5	2 86	2 861	451
5	2 77	2 782	333
		2 770	620
		2 762	403
2	2 68	2 677	271
5	2 59	2 577	124
		2 573	204
5	2 44	2 446	163
		2 443	343
1	2 38	2 383	711, 044
		2 374	324
10	2 28	2 288	453
		2 286	404
		2 273	642
		2 271	363
5	2 24	2 249	054
		2 233	613
		2 230	154
10	2 20	2 202	344
		2 197	480
		2 191	722
10	2 09	2 095	354
		2 094	125
		2 092	205
		2 086	444
		2 081	215
		2 080	524

CeT$_4$

I/*I* vis	*d* (obs)	*d* (calc)	*hkl*
5	10 46	10 71	001
10	9 51	9 51	011
100	8 76*b*	8 92	120
		8 77	200
2	6 76	6 853	121
2	6 35	6 448	211
5	5 70	5 801	031
2	5 37	5 353	002
10	5 07	5 089	320
100	4 54*b*	4 590	321 122
		4 569	202
		4 505	141
15	4 18	4 180	222
30	4 05	4 058	401
30	4 00	4 038	420
		3 984	411
15	3 86	3 875	340
		3 867	051
10	3 73	3 722	042
15	3 68	3 689	322
1	3 41	3 426	242
20	3 33	3 347	440
		3 323	520
		3 314	123
5	3 20	3 224	351
		3 194	441
5	2 90	2 900	451
15	2 81	2 823	522
		2 813	620
		2 794	611
5	2 71	2 714	271, 460
10	2 60	2 599	362
10	2 55	2 564	371 124
		2 561	204
10	2 46	2 461	560
		2 454	353
10	2 37	2 378	044
		2 370	324
		2 357	144
15	2 29*b*	2 298	642
		2 285	404
		2 284	363
		2 278	073
10	2 26	2 255	740
		2 248	613
		2 243	173
10	2 23	2 236	562
		2 231	660
		2 230	480
15	2 20	2 216	722
		2 203	344
1	2 15	2 148	633
15	2 08	2 085	524
		2 082	125
		2 080	205
		2 072	643
		2 070	215
10	2 02	2 028	802 760
		2 021	1 01 1
		2 018	840

PuT$_4$

I/*I* vis	*d* (obs)	*d* (calc)	*hkl*
5	10 65	10 71	001
10	9 66	9 51	011
100	8 92*b*	8 92	120
		8 77	200
10	7 32	7 45	021
10	6 43	6 45	211
15	5 71	5 80	031
15	5 06	5 09	320
80	4 55	4 59	321 122
		4 57	202
		4 50	141
15	4 45	4 46	212
		4 46	240
2	4 17	4 18	222
25	4 01	4 04	420
		3 98	411
5	3 86	3 88	340
		3 87	051
25	3 68	3 69	322
1	3 51	3 52	013
		3 50	431
10	3 41	3 43	242
20	3 32	3 35	440
		3 32	520
		3 31	123
1	3 18	3 17	033
2	2 98	2 97	360
15	2 82*b*	2 82	522
		2 81	620
		2 79	611
2	2 71	2 71	271 460
15	2 56*b*	2 56	124 371
		2 56	204
15	2 46*b*	2 46	560
		2 45	353
10	2 37	2 38	044
		2 37	324
20	2 29*b*	2 30	642
		2 28	404
		2 28	363
		2 28	073
15	2 25	2 26	740
		2 25	613
		2 24	173
15	2 20	2 22	722
		2 20	344
5	2 15	2 15	633
20	2 08	2 08	524
		2 08	125
		2 08	205
		2 07	643
		2 07	215
2	2 05	2 06	482
		2 05	831
5	2 02	2 03	802 760
		2 02	1 10 1
		2 02	840

ThT_4, CeT_4, ZrT_4 and HfT_4 Thorium nitrate solution (purified by solvent extraction with TBP in xylene), zirconium nitrate (E Merck, reagent grade), ceric ammonium nitrate (E Merck, reagent grade) and hafnium nitrate solution (prepared from spectroscopically pure hafnium metal by dissolving in hydrofluoric acid precipitating as hydroxide and finally dissolving in nitric acid) were used for the preparation of these compounds following the same general procedure described for UT_4 In these cases, however, it was necessary to precipitate the complexes by dilution with water after mixing the alcoholic solutions of the reagents Most of the precipitates were recrystallized in benzene to yield crystals of suitable size for single-crystal X-ray analysis

PuT_4 High purity plutonium metal was dissolved in hydrochloric acid and oxidized to the tetravalent state by addition of several drops of nitric acid The solution was taken up in alcohol and treated with slightly less than the calculated amount of TTA (also in a water-alcohol solution) to give PuT_4 The precipitate was filtered and washed with distilled water and alcohol and finally recrystallized from benzene

Analysis

With the exception of PuT_4, all the compounds were analysed by careful ignition and weighing of the resulting oxides Analysis in all cases corresponded to the formula MT_4, where M stands for the metal and T for the ionized TTA On the basis of its X-ray powder pattern, which is very similar to those of the other compounds, the TTA chelate of Pu is presumed to have a comparable formula (PuT_4)

Apparatus

Single-crystal X-ray studies were made on UT_4, ThT_4, HfT_4, ZrT_4 and CeT_4 using the Buerger precession camera and MoK_α radiation (0 7107 Å) Precession photograph measurements were corrected for film shrinkage Zero and upper level phorographs were taken of CeT_4 using a Weissenberg camera Powder photographs were taken of all the compounds with CuK_α radiation (1 5418 Å) The powder patterns were not corrected for film shrinkage owing to the absence of visible reflexions in the back-reflexion region

Infra-red spectra were recorded on a Perkin-Elmer Model 421 infra-red Spectrophotometer employing the KBr pellet technique Nujol mulls were not used However, there was no change in the spectra using the KBr method, indicating that no exchange of Br took place with T

Differential thermal analysis curves were obtained with a R L Stone Model DS-2 Differential Thermal Analyser using a dynamic oxygen atmosphere and a heating rate of 10 C/minute

The number of molecules per unit cell was determined from the observed density values These were obtained by precisely suspending single crystals in an aqueous solution of thallium formate and determining the density of the solution pycnometrically

RESULTS

X-ray crystallographic data

Single crystal studies established the isomorphism of the five TTA chelates investigated Using data obtained from the single-crystal photographs, powder photographs of all the compounds were indexed Calculated interplanar spacings were only given for those (*hkl*) reflexions which appeared on the Weissenberg and precession photographs Powder diffraction data for the six compounds are given in Table 1 and clearly reveal the isomorphism of the compounds

X-ray crystallographic data on these compounds are listed in Table 2 With the exception of PuT_4, the values were derived from single-crystal photographs Lattice constants of PuT_4 were presumed to be essentially identical to those of CeT_4, because of the virtual equivalence of the two diffraction patterns (see Table 1)

The length of the *c*-axis changes very little in the series of six compounds The length of the *b*-axis varies somewhat more, and that of the *a*-axis most Although the unit cell volumes fall within a relatively narrow range, there appears to be a direct

TABLE 2 —X-RAY CRYSTALLOGRAPHIC DATA

Orthorhombic, Z = $4(C_{32}F_{12}H_{16}MO_8S_4)$

Compound	a(Å)	*b*(Å)	*c*(Å)	Unit cell Volume (A3)	Density Calc (g/cm³)	Density Obs (g/cm³)
UT_4	17 701	20 446	10 736	3885 5	1 919	1 87
ThT_4	17 842	20 630	10 698	3937 7	1 883	1 89
HfT_4	17 258	20 393	10 794	3798 9	1 859	1 80
ZrT_4	17 271	20 422	10 779	3801 8	1 705	1 67
CeT_4	17 532	20 719	10 710	3890 4	1 749	1 76
Put_4	17 53	20 72	10 71	3890	1 92	—

correlation between the metal covalent radius and either the cell volume or the *a*-axis length Thorium and uranium have somewhat larger covalent radii than either hafnium or zirconium(9,10) and this appears to be reflected in the cell volumes of their respective TTA chelates

Buerger precession photographs were taken of crystals of each compound along the three major crystallographic axes All corresponding patterns exhibited identical symmetry and showed the same systematic extinctions A CeT_4 crystal, representative of the other compounds, was further investigated with a Weissenberg camera Oscillation and Weissenberg patterns were obtained with the *a*-axis of the crystal oriented parallel to the camera oscillation axis Equi-inclination photographs were taken of eight higher levels

The precession photographs taken along the three major axes all showed two fold rotations around the centre together with a mirror reflexion All of the photographs exhibited the same systematic absences, namely reflexions of the type (*h*0l) with *h* odd, (*hk*0) with *k* odd, (*h*00) with *h* odd, and (0*k*0) with *k* odd The probable space groups are either D_2^3-$P2_12_12$ or C_{2v}^4-Pma2 More investigation is needed before an unequivocal assignment can be made to one of these two space groups

Optical examination

Optical examination of the crystals of the various compounds confirmed the fact that they were orthorhombic ZrT_4 and HfT_4 were colourless, ThT_4 pale yellow, UT_4 and PuT_4 brown, and CeT_4 deep reddish brown The observed colours agree with those reported for ThT_4 and ZrT_4, but not with the green colour reported for UT_4 (11) The UT_4 crystals show pronounced pleochroism, with colours ranging from deep brown to straw yellow The pinacoidal and prismatic faces were best developed in all of the crystals No signs of twinning were observed

Even the coloured crystals were sufficiently translucent to permit determination of their refractive indices Optical data on the compounds are listed in Table 3 The

(9) L PAULING, *Nature of the Chemical Bond*, Cornell University Press Ithaca, New York (1939)

(10) A F WELLS, *Structural Inorganic Chemistry*, (3rd Ed) Oxford (1961)

(11) E L ZEBROSKI, U S A E C Report BC-63 (1947)

TABLE 3—OPTICAL DATA

Compound	UT_4	ThT_4	HfT_4	ZrT_4	CeT_4	PuT_4
Colour	Brown	Pale yellow	Colourless	Colourless	Reddish brown	Brown
Refractive indices (Tungsten lamp, 25°C)						
α	1.564 ± 0.003	1.534 ± 0.003	1.537 ± 0.003	1.537 ± 0.003	1.602 ± 0.004	—
β	1.658 ± 0.004	1.626 ± 0.004	1.656 ± 0.004	1.656 ± 0.004	1.678 ± 0.005	—
γ	1.792 ± 0.004	1.810 ± 0.005	1.809 ± 0.005	1.809 ± 0.005	1.803 ± 0.006	—
Average index $\sqrt[3]{(\alpha, \beta)}$	1.669	1.653	1.664	1.664	1.692	
Pleochroism	Pronounced	None	None	None	*	—
α	Deep brown	—	—	—	—	—
β	Light brown	—	—	—	—	—
γ	Straw yellow	—	—	—	—	—
Optic axial angle (Calc from α, β & γ)	80 ± 8	70 ± 7	82 ± 8	82 ± 8	76 ± 8	—
Sign of double refraction	Positive	Positive	Positive	Positive	Positive	—
Acute bisectrix, Bx_a	γ	γ	γ	γ	γ	—
Optic orientation						
α	*a*	*a*	*a*	*a*	*a*	—
β	*b*	*b*	*b*	*b*	*b*	—
γ	*c*	*c*	*c*	*c*	*c*	—

* The deep colour of CeT_4 makes it difficult to determine whether or not it is slightly pleochroic

average refractive index varies relatively little in the series, demonstrating the equalizing influence of the predominant TTA component The average refractive index of pure TTA is about 1 51

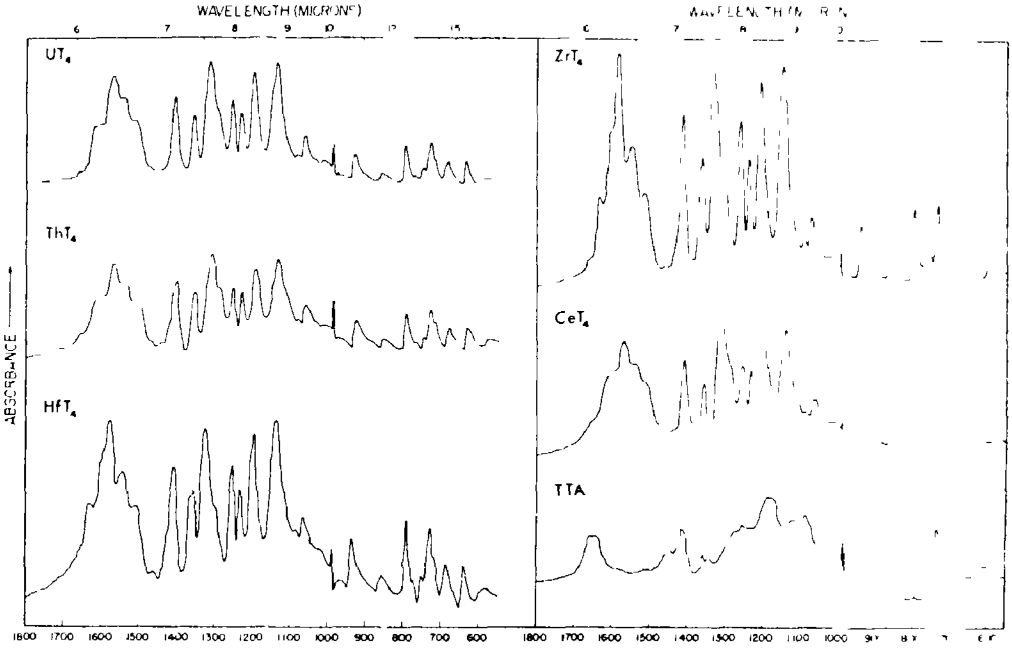


FIG. 1 —Infra-red absorption spectra

Infra-red spectra

The infra-red spectra of certain β-diketones and some of their metallic chelates, particularly the acetyl-acetonates, have been investigated previously[12-18] The infra-red spectra of TTA and its chelates with tetravalent uranium, thorium, zirconium hafnium and cerium in the region 1800–550 cm^{-1} are given in Fig 1 and the frequencies at which the absorption peaks occur are listed in Table 4 The infrared spectra of the compounds investigated show strong similarities with little variation in the frequencies of their absorption bands As was reported by FERRARO and HEALY[19], who investigated the infra-red spectra of ThT_4 and UO_2T_2, the spectra are complex in nature and the strong absorption in the area 1650–1550 cm^{-1} is due to the carbonyl vibration Whereas for pure TTA this absorption occurs as a single band at 1650 cm^{-1} in the case of the five metallic chelates investigated there is a splitting of the band as well as a shift to lower frequencies This shift to lower frequencies is in agreement with the results previously reported for the metallic chelates with acetylacetone and is attributed to the formation of M—O bands

[12] R RASMUSSEN, D D TUNNICLIFF and R R BRATTAIN, *J Amer Chem Soc* **71**, 1068 (1949)
[13] J LECOMTE, *Disc Faraday Soc* **9**, 125 (1950)
[14] C DUVAL, R FREYMANN and J LECOMTE, *Bull Soc Chim (France)*, **19**, 106, (1952)
[15] H W MORGAN, U S A E C Document 2659 (1949)
[16] L J BELLAMY and R F BRANCH, *J Chem Soc* 4491 (1954)
[17] R L BELFORD, A F MARTELL and M J CALVIN, *J Inorg Nucl Chem* **2**, 11 (1956)
[18] R WEST and R RILEY, *J Inorg Nucl Chem* **5**, 295 (1958)
[19] J R FERRARO and T V HEALY, *J Inorg Nucl Chem* In press (1962)

TABLE 4 INFRA-RED ABSORPTION PEAKS

TTA	UT_4	ThT_4	HfT_4	ZrT_4	CeT_4
(cm^{-1}) *I*	(cm^{-1}) *I*	(cm^{-1}) *I*	(cm^{-1}) *I*	(cm^{-1}) *I*	(cm^{-1}) *I*
1650 *m*					
	1620 *m*	1620 *m*	1633 *s*	1632 *m*	1600 *m*
	1568 *s*	1570 *vs*	1578 *vs*	1579 *vs*	1569 *s*
	1535 *m*	1540 *s*	1540 *s*	1545 *m*	1534 *s*
	1508 *m*	1505 *m*	1510 *s*	1512 *m*	1508 *m*
1450 *m*					
1414 *s*	1405 *s*	1404 *s*	1409 *s*	1410 *s*	1408 *s*
1358 *m*	1355 *m*	1355 *m*	1358 *s*	1358 *m*	1355 *m*
1343 *m*					
	1315 *vs*	1308 *vs*	1327 *vs*	1327 *vs*	1309 *vs*
1255 *s*	1254 *s*	1252 *m*	1252 *s*	1255 *s*	1252 *s*
	1230 *m*	1230 *m*	1233 *s*	1234 *m*	1230 *m*
	1196 *s*	1194 *s*	1198 *s*	1200 *s*	1196 *s*
1180 *vs*					
	1136 *vs*	1136 *vs*	1140 *vs*	1140 *vs*	1135 *vs*
1115 *s*					
1085 *s*	1082 *w*	1080 *w*	1088 *m*	1088 *w*	1084 *w*
	1063 *m*	1060 *m*	1066 *m*	1068 *w*	1062 *m*
	1012 *w*	1010 *w*	1015 *m*	1020 *w*	1015 *w*
972 *m*					
932 *w*	930 *w*	928 *w*	937 *m*	938 *w*	930 *w*
848 *w*	860 *w*	855 *w*	860 *w*	862 *w*	858 *w*
	796 *w*	796 *m*	796 *m*	792 *w*	796 *w*
736 *s*	730 *w*	730 *m*	730 *m*	732 *w*	730 *m*
672 *w*	684 *w*	680 *w*	687 *w*	690 *w*	680 *w*
629 *m*	636 *w*	632 *w*	640 *w*	640 *w*	645 *w*
	580 *w*	578 *w*	580 *w*	588 *w*	578 *w*

vs = very strong, *s* = strong, *m* = medium, *w* = weak

TABLE 5 — MELTING POINTS OBTAINED FROM DTA CURVES

Compound	Melting point (°C)*	Literature value (°C)
TTA	50	38-42†
UT_4	250	--
ThT_4	235	224 (11)
HfT_4	240	—
ZrT_4	240	229 (11)
CeT_4	190	—

* Values are accurate to ± 10°C

† Value given by manufacturer

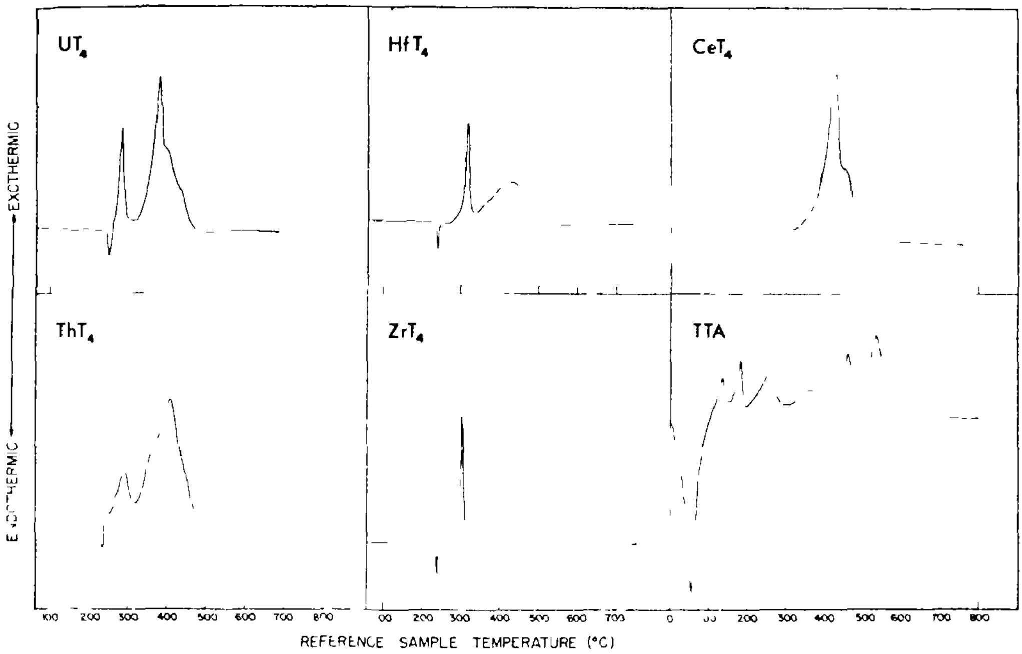


FIG. 2 DTA curves

Differential thermal analysis

Differential thermal analysis curves for the various compounds and pure TTA are shown in Fig 2 The endothermic peaks are assumed to represent melting, since the peaks for ThT$_4$ and ZrT$_4$ occur at temperatures close to those reported for the two compounds(11) Melting points of the compounds, based on the DTA studies, are listed in Table 5 along with a few literature values No reasons are apparent for the relatively low melting temperature of CeT$_4$ The exothermic peaks at around 300°C are thought to be associated with oxidation of sulphur, whereas those at 400–450°C are assumed to be caused by oxidation of CO and possibly carbon

Acknowledgement—The authors gratefully acknowledge the assistance of K M Abubacker, Chemistry Division, Atomic Energy Establishment, Trombay, Bombay, India, in the preparation of UT$_4$, ThT$_4$, ZrT$_4$ and CeT$_4$

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 1021 to 1031. Pergamon Press Ltd. Printed in Northern Ireland

AQUEOUS SYSTEMS AT HIGH TEMPERATURE—X

INVESTIGATIONS ON THE SYSTEMS UO_3–CuO–SO_3–D_2O, UO_3–NiO–SO_3–D_2O, AND UO_3–CuO–NiO–SO_3–D_2O, 260–410°C. LIQUID-LIQUID IMMISCIBILITY AND CRITICAL PHENOMENA*(1)

WILLIAM L. MARSHALL and ERNEST V. JONES
Reactor Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee

(*Received* 3 *December* 1962)

Abstract—With the use of the synthetic method, some phase boundaries of liquid–liquid immiscibility and critical phenomena (where $L = V$) were determined for the condensed systems UO_3–CuO–SO_3–D_2O, UO_3–NiO–SO_3–D_2O and UO_3–CuO–NiO–SO_3–D_2O at temperatures from 280 to 410°C, at SO_3 concentrations varying from 0.02 to 1.0 molal, and at varying molal ratios, UO_3/CuO/NiO. With some of these results, combined with previous data, three-dimensional models were constructed which specified the saturating phases or critical phenomena, and the variation in phase boundaries as a function of temperature (260–430°) and composition (0.02–1.0 molal SO_3) for the four-component systems UO_3–CuO–SO_3–D_2O and UO_3–NiO–SO_3–D_2O. In the system containing CuO the second liquid phase predominated as a saturating phase at the higher temperatures and extended from the system UO_3–SO_3–D_2O to CuO–SO_3–D_2O whereas, for the system containing NiO the solid, $NiSO_4 \cdot D_2O$, was the predominant saturating phase. In both systems a critical surface was defined over which maximum molal ratios, Σ (metallic oxide)/SO_3, varying from 0.3 to 0.5 were observed. In the two liquid phase regions, as an approximation, CuO, NiO, or both can be stoicheiometrically substituted for UO_3 in small amounts in a particular composition without changing appreciably the temperature of liquid–liquid immiscibility.

LIQUID–LIQUID immiscibility and high concentrations of metallic oxide component in the supercritical fluid have been found previously in the condensed systems UO_3–SO_3–H_2O, UO_3–SO_3–D_2O and CuO–SO_3–D_2O at temperatures between 270 and 430°C.(2) The results of these investigations have been of use in the selection of fuel compositions for aqueous homogeneous reactors. Of more value would be systematic information on the boundary regions of liquid–liquid and liquid–solid equilibria, and critical phenomena (where $L = V$) of systems containing all the primary components of a reactor fuel. These systems involve UO_3 as the fuel component, CuO as a component utilized for the catalytic recombination of radiolytic H_2 and O_2, and NiO which dissolves into solution as a corrosion product of stainless steels.

The purpose of this study, therefore, was to provide sufficient phase equilibrium data, obtained in a systematic manner, for establishment of solution and solid (or second liquid phase) compositions, and critical phenomena over a wide variation of concentration and temperature. Some of these phase boundaries are presented for portions of the systems UO_3–CuO–SO_3–D_2O, UO_3–NiO–SO_3–D_2O, and UO_3–CuO–NiO–SO_3–D_2O. When part of this information is combined with previous data for the separate three-component systems UO_3-SO_3-D_2O,(2) CuO-SO_3-D_2O,(2) and NiO-SO_3-D_2O,(3) the four-component systems UO_3-CuO-SO_3-D_2O and UO_3-NiO-SO_3-D_2O at 300°C,(4) and with some additional data presented herein, three-dimensional models can be constructed to describe portions of the four-component systems as a function of temperature.

---

* This paper is based on work performed at Oak Ridge National Laboratory, which is operated by Union Carbide Corporation for the U.S. Atomic Energy Commission.

(1) Previous Paper in Series: "The System Li_2SO_4–H_2SO_4–H_2O and its D_2O Analogue, 200–350°C," W. L. MARSHALL, R. SLUSHER and F. J. SMITH, *J. Inorg. Nucl. Chem.* **25**, 559 (1963).

(2) W. L. MARSHALL, E. V. JONES, G. M. HEBERT and F. J. SMITH, *J. Inorg. Nucl. Chem.* **24**, 995 (1962).

EXPERIMENTAL

Reagents used were the same as described in previous papers of this series. The method of preparation of synthetic solutions was the same. All other experimental procedures were identical, the synthetic method(5) being used to define boundaries of liquid-liquid immiscibility and critical phenomena. The observations of a rapid reversibility with temperature of liquid-liquid immiscibility and critical phenomena were identical with those observations made previously.

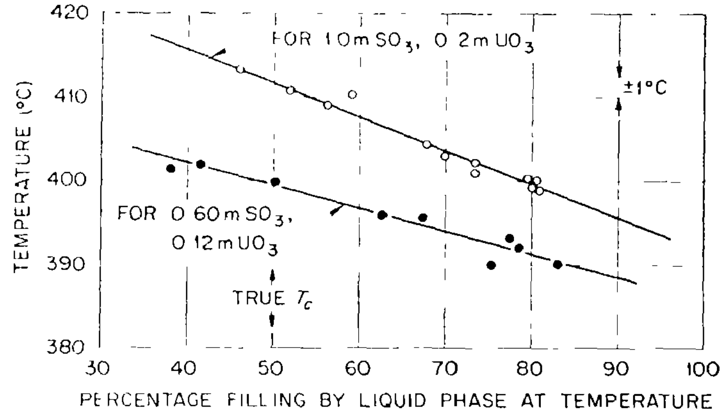


FIG. 1.—The effect of tube filling on the apparent critical temperature for solutions of SO_3, UO_3, and D_2O.

Since true critical phenomena, where liquid (L) becomes identical with vapour (V), are observed only when the volumes of the two phases are identical, it was of interest to determine apparent critical temperatures (where the meniscus became undetectable by visual observation) as a function of liquid-volume filling. The results for two solutions, 1.0 and 0.6 molal in SO_3, and both containing UO_3, plotted in Fig. 1, show a maximum difference of about 8 degrees between a 50 per cent and 70 per cent filling. For pure D_2O the difference in apparent critical temperature between these two limits would be about 1 degree.(6) Temperatures reported for critical phenomena were obtained for liquid fillings at temperature between these limits and, therefore, might be expected not to exceed an error of ±1 to ±2° at low concentrations of SO_3 and ±8° at 1 molal SO_3. For a single experiment it is difficult to adjust the liquid to vapour volume ratio at 25° to give a 50 per cent filling at the observed critical temperature.

RESULTS AND DISCUSSION

The four component systems UO_3-CuO-SO_3-D_2O *and* UO_3-NiO-SO_3-D_2O

When the additional component, CuO or NiO, is added to the system UO_3-SO_3-D_2O a further definition and restriction of composition must be made in order to retain simplicity in the presentation of the data. Previously, the molal ratio, *metallic oxide* m_{UO_3}, was defined as R_{I}, R_{Cu}, or R_{Ni} for the separate molal ratios.(4) A new symbol,

---

(3) W. L. MARSHALL, J. S. GILL and RUTH SLUSHER, *J. Inorg. Nucl. Chem.* **24**, 889 (1962).

(4) W. L. MARSHALL and J. S. GILL, *J. Inorg. Nucl. Chem.* **22**, 115 (1961).

(5) C. J. BARTON, G. M. HEBERT and W. L. MARSHALL, *J. Inorg. Nucl. Chem.* **21**, 141 (1961).

(6) G. M. HEBERT, H. F. McDUFFIE and C. H. SECOY, *J. Phys. Chem.* **62**, 431 (1958).

R, is now used for the summation of the separate ratios This and the previous ratios provided a means of showing conveniently on one plot the change with temperature of phase boundaries over a wide range of SO_3 concentration The additional restriction is that for any set of particular experiments another molal ratio, that of metallic oxides to each other, R(MO), as specific examples, m_{UO_3} $m_{CuO} = R(UO_3$ CuO$)$ or m_{UO_3} $m_{\text{additional metallic oxides}} = R(UO_3$ MO$)$, is kept constant Experiments on these restricted solution compositions provide a set of boundary curves of liquid–liquid immiscibility, critical phenomena, or precipitation of solid as a function of temperature, each *curve* representing conditions at a fixed concentration of SO_3 and value of R(MO) but at a variation of R The molality of SO_3 is changed for each curve but the value of R(MO) is changed only for each separate set of curves

The data experimentally obtained for the four-component systems UO_3–CuO–SO_3 D_2O and UO_3–NiO–SO_3–D_2O are included on Table 1, sets A and B are for the system containing CuO and sets C and D for that one containing NiO Included in the key to Table 1 are the values of R(MO) for each set Including the data previously presented on the separate three-component systems,(2 3) four sets each of data were then available for describing the system containing CuO and the one containing NiO, these being for $R(UO_3$ MO$)$ 1 0, 2 1, 1 1, and 0 1

Figure 2 shows the two new sets each of curves plotted from data in Table 1 for the two four-component systems, and includes values presented previously at $R = 0$ (2) In many experiments on solutions of high R and low $R(UO_3$ MO$)$ a very small amount of solid was observed to appear at several degrees below the reported temperature of liquid–liquid immiscibility In some experiments a large amount of solid appeared These observations are designated in Table 1, the temperatures of liquid–liquid immiscibility are still reported but represent the behaviour of liquid phase compositions along a liquid$_1$–liquid$_2$-solid phase boundary not too far removed from the solution compositions at 25°

From the curves, from some additional data given herein (Table 2), and from the data presented previously,(2 3 4) five drawings each were constructed to describe the CuO and NiO containing systems Each drawing showed isotherms of the phase boundaries plotted on two-dimensional, orthogonal axes of R_U against R_{Cu} or R_{Ni} at a fixed molality of SO_3

In the construction of these drawings some speculation was necessary to fill in certain areas where solid phases saturated the solution With respect to the separate three-component systems UO_3–SO_3–D_2O, CuO–SO_3 D_2O, and NiO–SO_3–D_2O there was little ambiguity Some solubilities of UO_3 hydrates in SO_3–H_2O at temperatures up to 350° have been presented previously (4 7) The solubility of UO_3 $\frac{1}{2}D_2O$ in SO_3–D_2O solutions was determined at 300° with J S GILL* and R SLUSHER* (Table 2) and showed little difference from those values in SO_3–H_2O The solubility of antlerite ($3CuO$ SO_3 $2D_2O$) in SO_3–D_2O was determined at 300, 325 and 350° with GILL (Table 2) and showed somewhat higher solubilities than in SO_3–H_2O solution Solubilities of two salts (CuO $3UO_3$ and $3CuO$ SO_3 $2D_2O$) in SO_3–D_2O solutions at 325 and 350° along an isothermally invariant curve (Table 2) were determined with GILL

---

* Reactor Chemistry Division, Oak Ridge National Laboratory

(7) F V JONES and W L MARSHALL, *J Inorg Nucl Chem* **23**, 287 (1961)

TABLE 1.—TEMPERATURES (°C) FOR THE APPEARANCE OF LIQUID-LIQUID IMMISCIBILITY AND CRITICAL PHENOMENA IN THE SYSTEMS UO_3-CuO-SO_3-D_2O, UO_3-NiO-SO_3-D_2O AND UO_3-CuO-NiO-SO_3-D_2O

Set	*R*	SO_3 (molality)						
		1.000	0.600	0.3000	0.2000	0.1000	0.0500	0.02000
A	1.000	276.6 L	277.7 L	282.2 L	287.3 L	289.8 L	308.6 L	310 S
	0.800	305.9 L	302.7 L	303.2 L	308.4 L	315.1 L	327.5 L	339.2 L
	0.600	340.5 L	334.2 L	329.9 L	331.4 L	334.6 L	343.8 L	348.5 L
	0.500	360.4 L	351.0 L	345.7 L	345.7 L	347.3 L	350.4 L	366.7 L
	0.400	379.3 L	370.8 L	—	—	—	—	—
	0.3000	394 C	388 C	378.2 L	372.9 L	371.5 L	368.9 L	374 C
	0.2000	398 C	390 C	381 C	380 C	378 C	375 C	374 C
	0.1000	404 C	395 C	385 C	380 C	376 C	375 C	374 C
B	1.000	233 S(BGr)	193 S(BGr)	267 S	238 S(BGr)	—	250 S	309 S
	0.800	309.2 L	306.2 L	307.3 L	311.3 L	—	330.3 L	285 S
	0.600	346.8 L	339.4 L	334.6 L	337.7 L	—	348.0 L	352.0 L
	0.500	—	—	351.7 L	—	—	—	—
	0.400	387.5 L	377.7 L	—	370.4 L	—	373.3 L	371.3 L
	0.3000	396 C	394 C	381.5 L	379.3 L	—	373 C	373 C
	0.2000	402 C	396 C	387 C	379 C	—	374 C	373 C
	0.1000	408 C	397 C	386 C	379 C	—	374 C	373 C
C	1.000	274.2 L	275.3 L	280.0 L	—	267 S(Gr)	290 S	—
	0.800	303.7 L	299.7 L S	301.0 L S	—	302.5 L S	290 S	—
	0.600	342.4 L	334.8 L + S	355.7 L S	—	330.8 L S	311.4 L	—
	0.500	363.1 L S	358.8 L S	353.4 L S	—	351.3 L S	331.2 L	—
	0.400	381.4 L S	373.7 L + S	379 C S	—	365.6 L S	362.7 L S	—
	0.3000	393.5 L	389.9 L	381 C + S	—	374 C	373 C	—
	0.2000	397 C	392 C	384 C	—	374 C	373 C	—
	0.1000	402 C	398 C	384 C	—	376 C	374 C	—
D	1.000	272.2 L + S	275.5 L + S(Gr)	280.3 L	—	250 S(Gr)	276 S(Gr)	—
	0.800	309.0 L + S	301.2 L + S	298.0 L	—	258 S(Gr)	287 S(Gr)	—
	0.600	348.3 L + S	337.2 L	329.1 L + S	—	267 S(Gr)	303 S(Gr)	—
	0.500	369.2 L	—	—	—	—	—	—
	0.400	—	375.7 L S	367.2 L	—	336.8 L S	307 S(Gr)	—
	0.3000	401 C	388 C	380 L	—	355.3 L	337.3 L S	—
	0.2000	404 C	391 C	383 C	—	369.4 L	352.5 L S	—
	0.1000	408 C	394 C	386 C	—	378 C	369.7 L + S	—

TABLE 1 (*Contd*)

E	1 000	275 5 L S	278 2 L	281 6 L - S	285 9 L	299 5 L — S(Or)	326 3 L — S	—
	0 800	307 7 L S	301 3 L	304 2 L S	300 4 L	305 4 L	327 5 L — S(Or)	—
	0 600	342 6 L — S	335 3 L S	326 7 L S	321 8 L - S	317 0 L — S	332 8 L	—
	0 500	361 8 L - S	352 6 L S	337 3 L S	335 3 L — S	330 0 L	338 0 L	—
	0 3000	400 C	387 C	374 7 L — S	367 2 L + S	365 3 L — S	364 6 L	—
	0 2000	398 C	391 C	380 C	377 C	374 C	374 C	—
	0 1000	404 C	394 C	381 C	378 C	376 C	373 C	—
F	1 000	275 6 L	276 3 L	280 8 L	286 2 L + S	306 0 L — S(Or)	342 0 L — S	—
	0 800	305 7 L + S	301 3 L	302 8 L	305 5 L	310 2 L — S	343 9 L — S	—
	0 600	344 0 L + S	334 9 L - S	332 5 L — S	334 8 L + S	331 2 L — S	350 9 L + S	—
	0 500	371 5 L — S	354 9 L — S	346 6 L S	345 8 L + S	342 9 L — S	355 2 L — S	—
	0 3000	397 C	390 C	378 2 L S	373 9 L	367 9 L — S	367 9 L	—
	0 2000	402 C	394 C	384 C	381 C	376 C	374 C	—
	0 1000	411 C	394 C	384 C	382 C	378 C	374 C	—
G	1 000	275 2 L	277 0 L S	284 7 L S	289 4 L — S	310 6 L S	<242 S	—
	0 800	310 0 L	304 6 L S	305 2 L	309 0 L — S	316 6 L	<248 S	—
	0 600	352 8 L	340 2 L	335 4 L	335 8 L	333 6 L	<332 S	—
	0 500	374 5 L	359 2 L	350 6 L	348 7 L	346 9 L	345 1 L — S	—
	0 3000	393 C	389 C	379 7 L	378 L C	374 C	372 C	—
	0 2000	398 C	392 C	381 C	379 C	375 C	374 C	—
	0 1000	399 C	392 C	380 C	378 C	375 C	375 C	—
H	1 000	280 1 L S*	287 4 L S*	294 9 L S	302 6 L S	<249 S	<248 S	—
	0 800	312 7 L S*	310 4 L - S*	314 2 L S	316 8 L S	317 5 L S	<240 S	—
	0 600	357 2 L S	350 5 L S*	340 1 L S	339 4 L - S	339 1 L	341 1 L S	—
	0 500	379 8 L S	370 1 L S	357 2 L	354 7 L	351 5 L	350 6 L + S	—
	0 3000	396 C	385 C	382 C	379 C	375 C	373 C	—
	0 2000	398 C	391 C	382 C	378 C	375 C	374 C	—
	0 1000	404 C	393 C	383 C	379 C	376 C	375 C	—

KEY

R $\frac{\Sigma \text{ metallic oxide (molality)}}{SO_3 \text{ (molality)}}$

L Appearance of second liquid phase

S Appearance of small amount of solid phase 1 to 10 below temperature of L,

Or orange Gr green, BGr blue-green

S* Appearance of abundant amount of S below temperature of L

C Observation of critical phenomena (L V)

UO_3 CuO NiO (Molal Ratio) in Sets

(A)	3 1 0	(E)	8 1 1				
(B)	1 1 0	(F)	4 1 1				
(C)	3 0 1	(G)	2 1 1				
(D)	1 0 1	(H)	1 1 1				

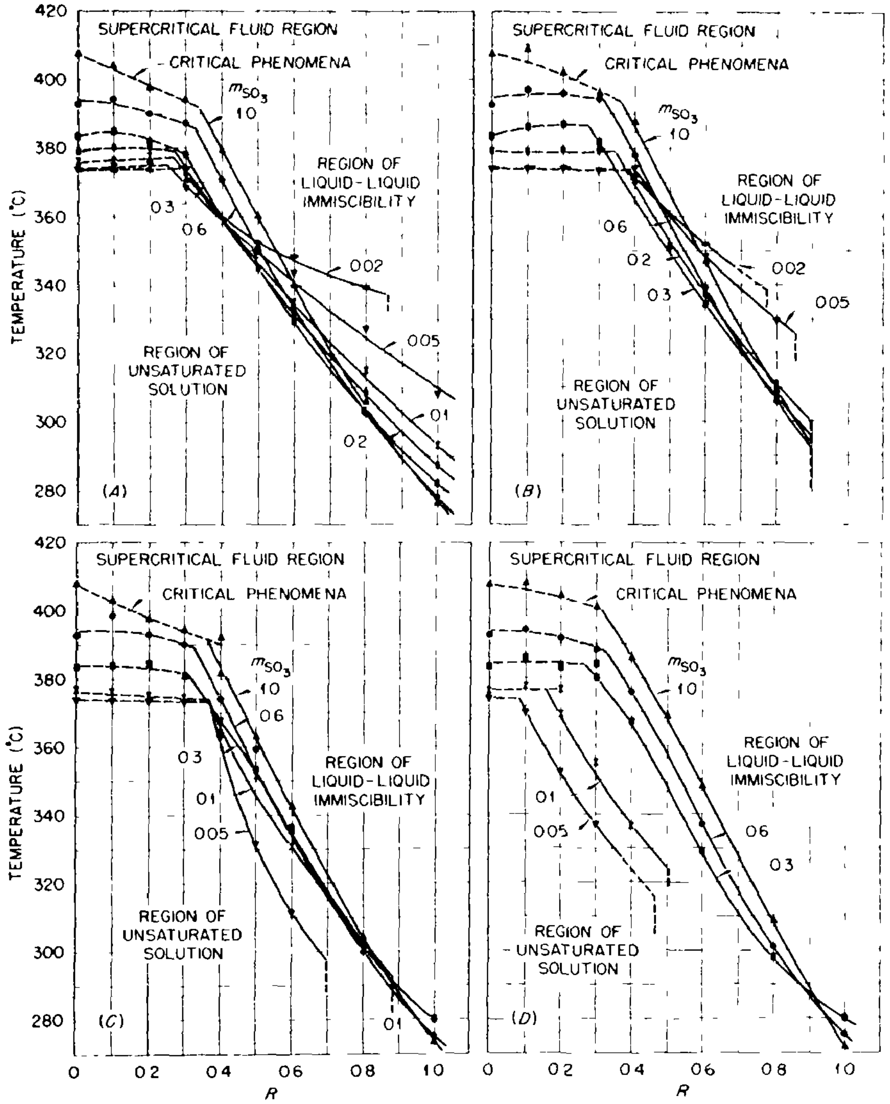


FIG 2 —Liquid-liquid immiscibility and critical phenomena in the systems UO_3 CuO SO_3-D_2O (Sets A and B) and UO_3 NiO-SO_3-D_2O (Sets C and D), 260–410 C (Key R $\Sigma m_{\text{metallic oxides}}/m_{SO_3}$, In Sets A, m_{CuO}/m_{UO_3} 0·333 B, m_{CuO}/m_{UO_3} = 1, C, m_{NiO}/m_{UO_3} = 0·333, D, m_{NiO}/m_{UO_3} 1)

and showed little change in $R(UO_3$ CuO) with temperature at constant molality of SO_3

From isotherms, selected from one drawing only, the dimensions were obtained from which a three-dimensional model could be constructed to show the variation of phase boundaries both as a function of R_{metal} for each of the metallic oxide components and as a function of temperature A series of these models was constructed from wood and showed the variation of phase boundaries at molalities of SO_3 of 0·0200, 0·0500, 0·100, 0·500 and 1·00.

Drawings made from photographs of the five models each of the two systems UO_3-CuO-SO_3-D_2O and UO_3-NiO SO_3-D_2O are shown in Fig 3 Each model shows the region of solution unsaturation and its boundaries where specified solid phases or second liquid phases saturated the liquid phase, or where critical phenomena

TABLE 2 —SOME SOLUBILITIES IN THE SYSTEMS UO_3—SO_3—D_2O, CuO—SO_3—D_2O AND UO_3—CuO—SO_3—D_2O, 300-350 C

SO_3 (molality)	R_U	Saturating phases
A System UO_3 SO_3-D_2O At 300 C		
0.0471	0.976	A^a
0.0470	0.972	A^a
0.0281	0.945	A^a
0.0272	0.956	A^a
0.0186	0.910	A^a
0.0150	0.890	A^a
0.0097	0.86	A^a
0.0051	0.82	A^a
0.0032	0.74	A^a
0.0029	0.73	A^a
0.0015	0.62	A^a
0.0012	0.68	A^a
B System CuO SO_3 D_2O At 300 C		
1.460	0.800	B
1.063	0.769	B
0.971	0.754	B
0.769	0.731	B
0.701	0.725	B
0.578	0.711	B
0.476	0.697	B
0.341	0.671	B
0.1568	0.620	B
0.0937	0.619	B
0.0258	0.548	B
0.00139	0.362	B
0.00132	0.325	B E
0.00128	0.314	B F
0.00117	0.334	B E

SO_3 (molality)	R_U	Saturating phases
B System CuO SO_3-D_2O (Contd) At 325 C		
0.385	0.690	B^a
0.348	0.681	B^a
0.333	0.667	B^a
0.322	0.669	B^a
0.140	0.614	B
0.0900	0.594	B^a
0.0208	0.522	B^a
0.00139	0.337	B^a - E^a
0.00139	0.296	B F
0.00113	0.329	B^a E^a
At 350 C		
0.273	0.608	D
0.255	0.612	D
0.1762	0.596	D
0.0972	0.575	D
0.0745	0.579	D - B^a

SO_3 (*m*)	R_U	R_{Cu}	Saturating phases
C System UO_3 CuO-SO_3 H_2O At 325 C			
0.0305	0.364	0.308	B C
0.0275	0.375	0.313	B C
0.0225	0.338	0.329	B C
At 350 C			
0.0308	0.347	0.296	B^a C^a
0.0302	0.371	0.311	B^a C^a
0.0297	0.381	0.311	B^a C^a

KEY $R_U = \frac{m_{UO_3}}{m_{SO_3}}$, $R_{Cu} = \frac{m_{CuO}}{m_{SO_3}}$

A UO_3 $\frac{1}{2}D_2O$, B Antlerite (3CuO SO_3 $2H_2O$ or 3CuO SO_3 $2D_2O$)

C CuO $3UO_3$, D Second Liquid Phase

F Unknown a copper oxy-suphate, $Cu(OH)_2$ or CuO

Where marked with an "a" the solid phases were determined by comparison of X-ray diffraction patterns, otherwise they were estimated from the behaviour of the system and past observations were observed, for compositions containing a fixed concentration of SO_3 Not onl can the solubility limits be defined but, by simultaneous examination of the series (models, the variation in surface areas for the different solids which saturate the solution phase can be compared In this respect, in all models the linear distance for on unit of R (at constant temperature) is the same, the temperature scale is also identica *Therefore, distances on the models are directly comparable* by dimension on the basi

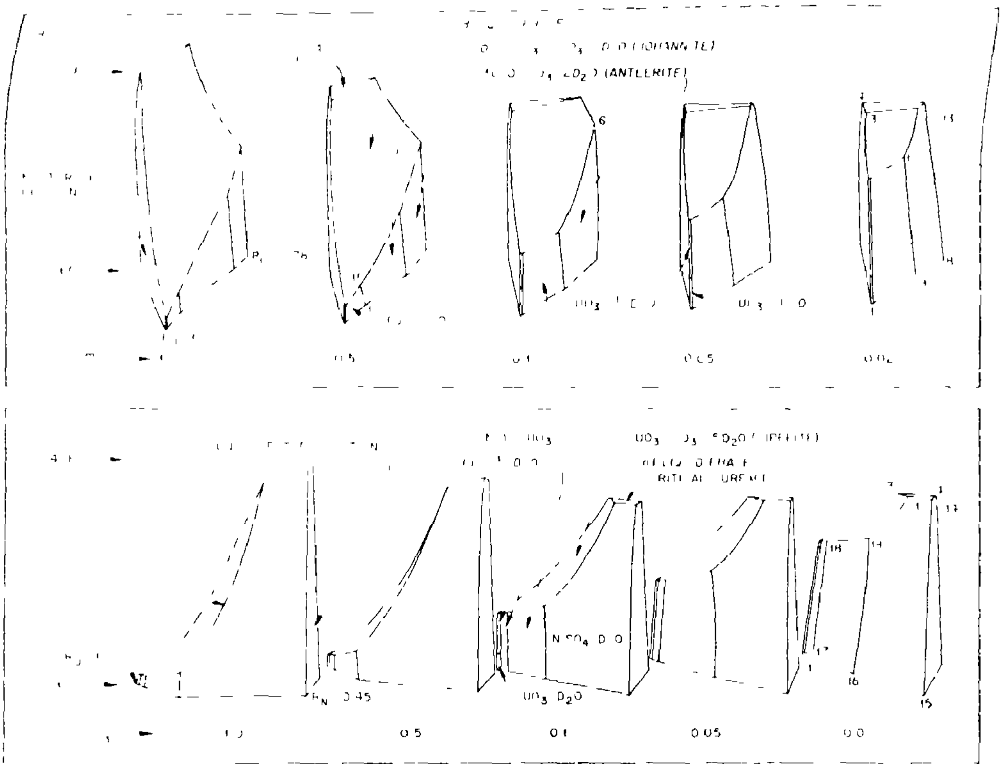


FIG 3 - Drawings of three-dimensional models showing the surfaces of saturation and critical phenomena for the systems UO_3-CuO SO_3-D_2O (*A*) and UO_3 NiO-SO_3-D_2O(*B*)

of R (and T) but *not* on the basis of molality of components Otherwise, lengths along these scales on the model depicting phase boundaries for solutions 0 02 molal in SO_3 would be roughly 1/50 those of the model for compositions 1 0 molal in SO_3

Although some temperatures of two-liquid phase formation are given in Table 1 with the notations that solid formed at lower temperature, only those temperatures for which solid was not observed were used in construction of the models These boundaries of liquid liquid immiscibility then fitted well with the data on solid–liquid equilibria, obtained by sampling of solution phases at temperature Upon consideration of these various studies and results presented previously, the extent of solution saturation is believed to be well defined although the location of a few of the boundaries between different solid phases may not be exact

Upon inspection of the models there are several points of interest Firstly, the proportional area of liquid–liquid immiscibility is seen to increase as the concentration of SO_3 increases, both for the system containing CuO and that one containing NiO. Secondly, the lowest temperatures of liquid–liquid immiscibility decrease with increasing SO_3 concentration. Thirdly, for the system containing CuO, the surface area of liquid–liquid immiscibility extends from the system UO_3–SO_3–D_2O to CuO–SO_3–D_2O and, at the higher concentrations of SO_3, covers proportionally the largest area. In contrast, the areas of liquid–liquid immiscibility in the system containing NiO never extend to the system NiO–SO_3–D_2O and cover a proportionally smaller area, the predominant saturating phase is the solid $NiSO_4$ D_2O. These observations might be

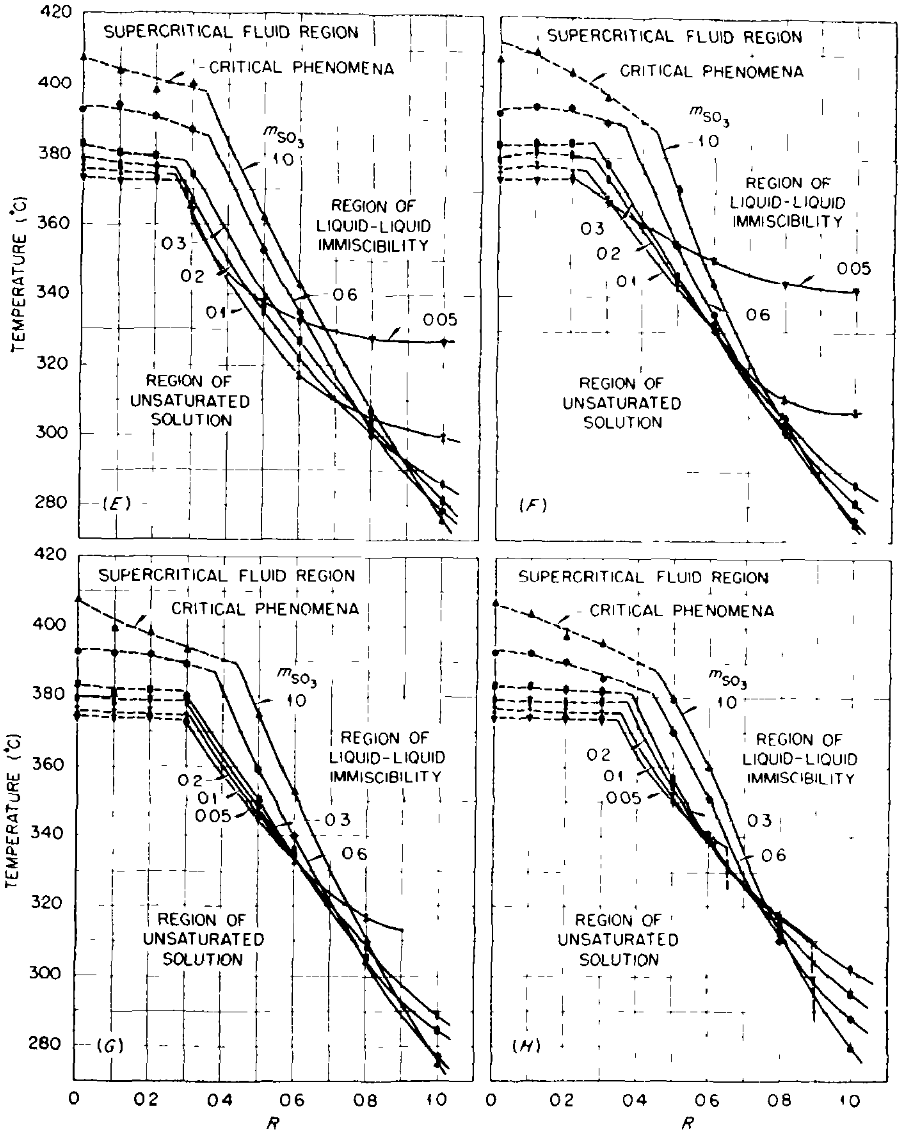


FIG. 4 – Liquid-liquid immiscibility and critical phenomena in the system UO_3 CuO–NiO-SO_3-D_2O (Sets E, F, G, H), 260–410 C (Key R $\Sigma m_{\text{metallic oxides}}$ m_{SO_3}, molal ratio (UO_3 CuO NiO) in sets E, 8 1 1, F, 4 1 1 G, 2 1 1, H, 1 1 1)

TABLE 3. SELECTED CO-ORDINATES FOR BOUNDARY REGIONS OF SATURATED SOLUTIONS AT CONSTANT CONCENTRATIONS OF SO$_3$ IN SYSTEMS UO$_3$–CuO–SO$_3$–D$_2$O AND UO$_3$–NiO–SO$_3$–D$_2$O

Point[a]	Co-ordinates[b]	Point[a]	Co-ordinates[b]
I. *System* UO$_3$–CuO–SO$_3$–D$_2$O		8	260, 0, 0.58
(1.000)[c]		9	260, 0.42, 0.33
1	260, 1.25, 0	12	347, 0.43, 0.29
2	267, 1.24, 0	13	373, 0.14, 0.38
3	395, 0.35, 0		
4	408, 0, 0	II. *System* UO$_3$–NiO–SO$_3$–D$_2$O	
5	427, 0, 0.32	(1.000)[c]	Co-ordinates[b,d]
6	340, 0, 0.77	14	413, 0, 0.13
8	260, 0, 0.78	15	260, 0, 0.45
9	260, 0.22, 0.63	16	260, 0.87, 0.32
10	260, 0.96, 0.15	17	260, 1.22, 0.030
11	275, 0.98, 0.15	18	267, 1.21, 0.025
12	315, 0.26, 0.62	19	276, 0.88, 0.31
(0.500)		20	320, 0.58, 0.32
1	260, 1.20, 0	21	398, 0.30, 0.14
2	272, 1.20, 0	(0.500)	
3	386, 0.31, 0	14	396, 0, 0.12
4	389, 0, 0	15	260, 0, 0.48
5	396, 0, 0.32	16	260, 0.87, 0.30
6	346, 0, 0.69	17	260, 1.16, 0.04
8	260, 0, 0.70	18	272, 1.16, 0.03
9	260, 0.36, 0.52	19	281, 0.89, 0.27
10	260, 0.88, 0.19	20	330, 0.55, 0.28
11	277, 0.90, 0.16	21	388, 0.26, 0.12
12	308, 0.39, 0.48	(0.1000)	
(0.1000)		14	376, 0, 0.12
1	260, 1.08, 0	15	260, 0, 0.52
2	298, 1.06, 0	16	260, 0.62, 0.33
3	376, 0.25, 0	17	260, 1.03, 0.04
4	376, 0, 0	18	297, 1.02, 0.03
5	379, 0, 0.51	19	307, 0.65, 0.25
6	360, 0, 0.63	20	340, 0.38, 0.24
8	260, 0, 0.65	21	375, 0.16, 0.12
9	260, 0.62, 0.34	(0.0500)	
12	302, 0.64, 0.31	14	374, 0, 0.11
(0.0500)		15	260, 0, 0.58
1	260, 1.03, 0	16	260, 0.51, 0.34
2	317, 0.98, 0	17	260, 0.97, 0.04
3	374, 0.32, 0	18	318, 0.91, 0.03
4	373, 0, 0	19	330, 0.54, 0.21
7	374, 0, 0.52	20	350, 0.37, 0.19
8	260, 0, 0.65	21	374, 0.20, 0.10
9	260, 0.53, 0.33	(0.0200)	
12	321, 0.57, 0.26	14	373, 0, 0.10
13	374, 0.06, 0.50	15	260, 0, 0.68
(0.0200)		16	260, 0.50, 0.40
1	260, 0.95, 0	17	260, 0.86, 0.07
2	340, 0.81, 0	18	341, 0.76, 0.03
3	373, 0.32, 0	19	348, 0.43, 0.18
4	372, 0, 0	20	360, 0.30, 0.15
7	373, 0, 0.43	21	373, 0.18, 0.09

(*a*) Designated on Fig. 3.

(*b*) Order: t(°C), R_U, R_{Cu} (or R_{Ni}).

(c) In parentheses: molality of SO$_3$.

(d) Co-ordinates of Points 1–4 are the same for both systems.

explained by speculating that $CuSO_4$ behaves in solution analogously to UO_2SO_4, considerable association to form non-ionic species may occur and thus enhance the probability of forming two liquid phases On the other hand, $NiSO_4$ may exist largely in the form of several ionic species, which would not be expected to favour the formation of immiscible liquids

The fourth point of interest lies with the supercritical surface over which the liquid phase becomes identical with vapour phase in all respects The vapour-pressure of the system for any composition on this surface is also defined uniquely as the critical pressure Nevertheless, in contrast to a one component system, upon increasing the temperature of the system above that at the critical point, but upon maintaining a constant pressure, a second liquid or solid phase may form from the supercritical fluid Fig 2 and the derived models give only the boundary limits at the critical temperature Of considerable interest, however, is the extent over which metallic oxides in one form or another are soluble in supercritical SO_3–D_2O (or in SO_3–H_2O)

Values of temperature and concentration at selected boundary points of saturation on each of the ten models have been documented and are presented in Table 3

The five component system UO_3–CuO–NiO–SO_3–D_2O

A simple description of the five-component system UO_3 CuO–NiO–SO_3–D_2O is exceedingly difficult Previously, part of the system was defined at a constant temperature of 300°⁽⁴⁾ In this present work, four sets of experimental data are given in Table 1 (Sets E, F, G, H) and define phase boundaries at values of R(UO_3 CuO NiO) of 8 1 1, 4 1 1, 2 1 1, and 1 1 1, respectively

These data and the previous values at $R = 0$,⁽²⁾ plotted in Fig 4, might be used to construct three-dimensional models depicting the phase boundaries in which the CuO and NiO components are combined—R(CuO NiO) is kept constant at 1 1—in order to correspond to a pseudo, single component

Simplification of phase boundaries of liquid–liquid immiscibility

If values of R are plotted against temperatures of liquid–liquid immiscibility at constant molality of SO_3 but for variations of R(MO)—(sets A–H)—then a series of curves is obtained which is not far removed from the boundary curve for the three-component system UO_3–SO_3–D_2O Plots of temperature against the mole fraction of $UO_3 = (m_{UO_3})\ (m_{UO_3} + m_{CuO} + m_{NiO})$ at constant m_{SO_3} and R have been made, as well as plots of R against mole fraction of UO_3 at constant m_{SO_3} and temperature As an approximation it appears that CuO, NiO, or both can be substituted for UO_3 until the mole fraction of UO_3 is lowered to about 0 7 with not more than a few degrees increase in temperature of liquid–liquid immiscibility at constant R, or with not more than about ±6 per cent change in R at constant temperature

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 1033 to 1040. Pergamon Press Ltd. Printed in Northern Ireland

AQUEOUS SYSTEMS AT HIGH TEMPERATURE—XI

EFFECT OF PRESSURE ON LIQUID-LIQUID IMMISCIBILITY IN THE SYSTEM UO_2SO_4–H_2O AND LIQUID-SUPERCRITICAL FLUID EQUILIBRIA IN THE SYSTEM UO_2SO_4–H_2SO_4–H_2O, 290–430°C, 75–330 BARS*(1)

WILLIAM L. MARSHALL and JAMES S. GILL
Reactor Chemistry Division, Oak Ridge National Laboratory,
Oak Ridge, Tennessee

(*Received* 3 *December* 1962)

Abstract—By making use of a visual method, the effect of hydrostatic pressures up to 320 bars in raising the temperature, in the vicinity of 300°C at saturation vapour-pressure, of second-liquid phase formation in the system UO_2SO_4–H_2O for solutions varying from 0.14 to 4.5 molal in UO_2SO_4 was found to be +0.082° per bar. One exploratory run each on a solution of UO_2F_2 and H_2O, and of $CuSO_4$, H_2SO_4 and H_2O, both of which show liquid–liquid immiscibility near 320° gave values of $(\partial t/\partial p)$ at constant composition of $\sim$+0.10 and +0.11, respectively. Since $(\partial t/\partial p)$ at a constant density of 0.712 for liquid H_2O at 300° is +0.093° per bar, the temperature of liquid–liquid immiscibility appears to show a strong dependency on solvent density. The effect of pressures up to 330 bars on the temperature of second-liquid phase formation from the supercritical fluid UO_3–SO_3–H_2O near 400° was found also to correspond approximately to $(\partial t/\partial p)$ at constant density for H_2O at the same initial pressure, the value being in the vicinity of +0.4° per bar. In some additional experiments the vapour-pressures for the deliquescence of solid UO_2SO_4 hydrate were found to vary from 120 bars at 345° to 305 bars at 425°.

FOR the use of aqueous, homogeneous reactor fuels containing UO_2SO_4 as the major component it was of interest to know the effect of hydrostatic pressure upon the temperature of second-liquid phase formation. For stoicheiometric UO_2SO_4 solutions in the presence of vapour, the temperatures of liquid–liquid immiscibility drop sharply from about 350° to a flat minimum at about 286°, and then increase slowly as the concentration of UO_2SO_4 increases. This phase boundary of liquid–liquid immiscibility and related boundaries in the system UO_3–CuO–NiO–SO_3–D_2O, of primary interest to homogeneous reactors, constituted upper limits for temperatures of the fuel. The effect of hydrostatic pressure (its magnitude and direction) on the temperatures of immiscibility not only would be of applied interest to the construction and operation of homogeneous reactors but might be related ultimately to some generalized solubility behavior of salts of these components in water solution.

This paper presents data on the effect of hydrostatic pressure on the temperatures of second-liquid phase formation of stoicheiometric UO_2SO_4–H_2O solutions at concentrations from 0.14 to 4.53 molal in UO_2SO_4, at temperatures from 286 to 318°

---

* This paper is based upon work performed at Oak Ridge National Laboratory, which is operated for the U.S. Atomic Energy Commission by Union Carbide Nuclear Corporation.

(1) Previous Paper in Series: "Liquid–Liquid Immiscibility and Critical Phenomena in the Systems UO_3–CuO–SO_3–D_2O, UO_3–NiO–SO_3–D_2O and UO_3–CuO–NiO–SO_3–D_2O, 260–410°C," W. L. MARSHALL and E. V. JONES, *J. Inorg. Nucl. Chem.* **25**, 1021 (1963).

and at pressures up to 320 bars Some additional data are presented which show the effect of pressure on the temperature of formation of heavy-liquid phases from supercritical, UO_2SO_4 H_2O fluids containing excesses of H_2SO_4 All data were obtained by visual observation through the use of glass tubes containing liquid phase compositions which could be pressurized by external means An empirical relationship of the temperature of formation to the solvent density is observed

EXPERIMENTAL

The preparations and analyses of stoicheiometric UO_2SO_4 solutions, of UO_2SO_4 solutions containing an excess of H_2SO_4 and of the solutions containing $CuSO_4$ and UO_2F_2, were carried out in the manner described previously(2,3) The reagents used in the preparations were the same The additional reagent UO_2F_2, was the same as used earlier(3)

Experiments were performed by the ordinary synthetic(4) and by a modified synthetic procedure In the modified method, using a glass-to-metal tube connector described in detail elsewhere,(5) a glass tube, connector and metal capillary tubing were filled with a solution of known composition The glass tube, sealed at the lower end and extending 15 cm down from the tube connector, was inserted into a molten-salt-bath apparatus described previously(4) The Vibrotool* was not attached and the connector was kept in the cool zone outside of the salt bath The contents of the tube were pressurized by means of an external high pressure assembly This pressure was measured on a bourdon type gauge† which was calibrated to ±0 1 per cent of reading by means of a dead-weight tester ‡

In the experimental procedure the solution within the tube was pressurized to a pressure, estimated from exploratory runs, which would not permit a second-liquid phase at the temperature of the salt bath The tube was then inserted into the bath, held at constant temperature, and the internal pressure slowly lowered until immiscibility was observed as evidenced by opalescence throughout the solution The pressure was then raised immediately and immiscibility disappeared This procedure was repeated several times at one temperature with a reproducibility in pressure reading of ±2 4 bars For further determinations the temperature was changed to another constant value and the lowering and consequent raising of pressure was then repeated to obtain another boundary limit of pressure and temperature If there was a delay in raising the pressure, the consequent macro-separation into an upper and lower liquid-layer, following the opalescence, prevented redetermination of the immiscibility point because of difficulty in remixing the two phases

In one series of experiments the pressure of water-vapour or supercritical fluid necessary to dissolve solid UO_2SO_4 hydrate at temperatures above 300° was determined by first adding powdered $UO_2SO_4\,3H_2O$ to a capillary tube At constant, high temperature the solid was pressurized slowly with pure water-vapour or supercritical fluid, and the pressure was recorded at which the solid first began to dissolve to form a liquid solution By lowering the pressure slowly, the reverse effect was observed and the point of formation of solid was recorded

RESULTS AND DISCUSSION

Effect of pressure on liquid-liquid immiscibility in the system UO_2SO_4–H_2O

In Table 1 are listed the pressure–temperature boundary data obtained in this investigation for stoicheiometric UO_2SO_4 solutions From these data it is seen that hydrostatic pressure has a significant effect on the temperature at which the second-liquid phase appears If the data are plotted separately for each concentration of

* Burgess Vibrocrafters, Inc , Grayslake, Ill , U S A

† Heise Bourdon Tube Co , Newton, Connecticut, U S A (16″ dia , 0–10,000 psi gauge)

‡ Manning, Maxwell and Moore, Inc , Stratford, Connecticut, U S A (Ashcroft Dead-Weight Tester)

(2) E V JONES and W L MARSHALL, *J Inorg Nucl Chem* **23,** 287, 295 (1961)

(3) W L MARSHALL, J S GILL and C H SECOY, *J Amer Chem Soc* , **76,** 4279 (1954)

(4) C J BARTON, G M HEBERT and W L MARSHALL, *J Inorg Nucl Chem* , **21,** 141 (1961)

(5) J S GILL and W L MARSHALL, *Rev Sci Instrum* **34,** 442 (1963)

TABLE I.—THE EFFECT OF PRESSURE ON THE TEMPERATURE OF LIQUID–LIQUID IMMISCIBILITY IN THE SYSTEM UO_2SO_4–H_2O

P(Bars)	t(°C)
(0 140)* †	
88‡	302
173	311
247	316
269	318
(0 280)	
80‡	295
135	300
155	302
157	303
203	305
226	308
243	309
272	312
304	314
(0 350)	
77	292
159	300
223	305
245	306
267	308
(0 580)	
70‡	286
104	290
142	292
160	293
201	296
(1 18)	
70†	286
121	290
145	292
158	293
223	298
263	301
324	306
(1 86)	
72‡	288
216	300
263	304
294	306
316	308
(2 60)	
74‡	290
101	292
134	295
162	297
215	301
258	304
270	306
310	308
(2 81)	
74‡	290
151	296
172	298
205	300
228	304
275	306
(3 54)	
78‡	293
129	296
150	298
184	300
213	303
235	305
280	308
298	310
316	311
(4 02)	
80‡	295
122	298
162	302
183	304
203	305
208	306
226	307
256	310
(4 53)	
124	304
160	306
188	309
223	312
253	314

---

* In parentheses molality of UO_2SO_4

† At molalities of UO_2SO_4 from 0 140 to 0 580, the heavy-liquid phase (L_2) appears upon lowering the pressure and at higher concentrations, the light-liquid phase (L_1)

‡ Estimated vapour-pressure at three phase equilibrium point $L_1 + L_2 + V$

UO_2SO_4 and are then compared, the following observations can be made

(1) The application of hydrostatic pressure at all concentrations of UO_2SO_4 *increases* the temperature of liquid–liquid immiscibility

(2) The change of temperature of appearance of a second liquid with pressure at a fixed concentration, x, of UO_2SO_4, i e $(\partial t/\partial p)_x$, is approximately constant regardless of whether the heavy-liquid phase (L_2) or light-liquid phase (L_1) is the one appearing from solution

After consideration of comments (1) and (2), all data were normalized by adjusting to a common curve, shown in Fig 1, of Δ(temperature) vs Δ(pressure) At Δt and

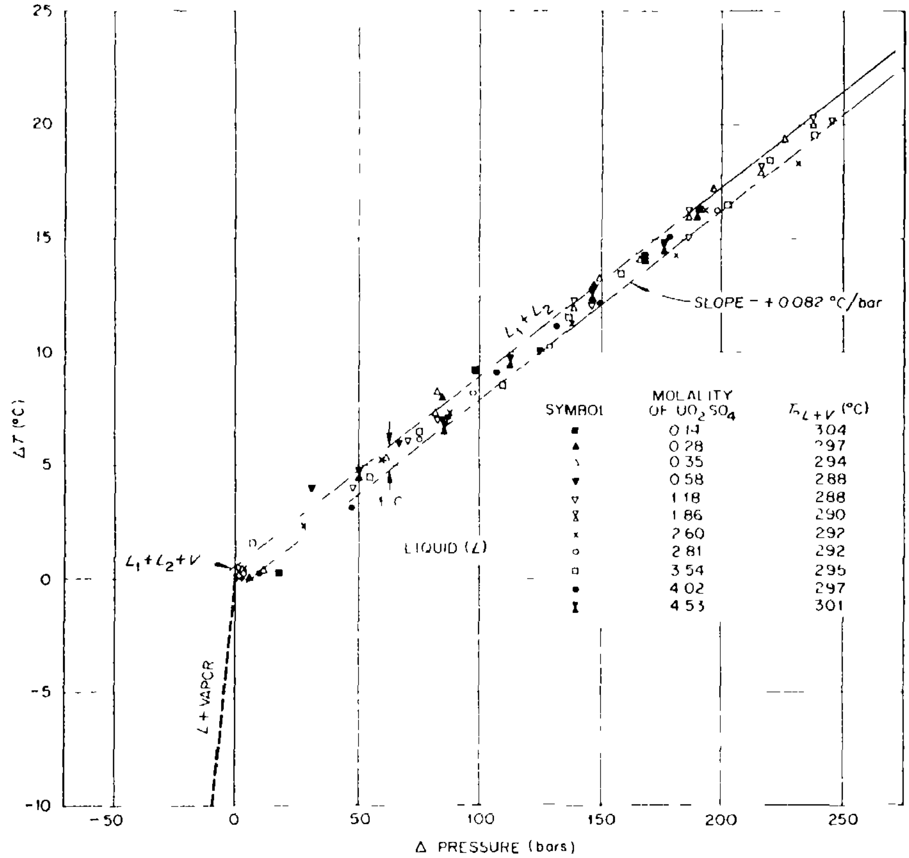


FIG 1 —The effect of hydrostatic pressure on liquid–liquid immiscibility for stoicheiometric UO_2SO_4 solutions (in H_2O) 11 separate runs (*Note added in proof* Subtract 2° from T_{2l+v} for corrected temperature)

$\Delta p = 0$ for each separate concentration of UO_2SO_4 the vapour-pressure and temperature is that at the three-phase invariant point $L_1 + L_2 + V$ The vapour-pressures of the various solutions at this point were estimated roughly to be close to that for H_2O (70 bars at 286° and 88 bars at 302°) and did not need to be known exactly since the lowering in vapour-pressure due to the solute was very small compared to the relative amount of hydrostatic pressure applied to the solution phase

If the values for change in temperature with pressure at constant density (d) of liquid water (L), i e, $(\partial t/\partial p)_d$, at the limit where vapour is present are determined by making use of other data,[6] then they vary from 0 086° per bar at 286° to 0 094° per bar at 302° The variation of temperature with pressure at constant density of liquid water is nearly linear at pressures from that of saturation vapour (the limit) to those much greater than 300 bars The average slope, $(\partial t/\partial p)_x$, for the $L_1 + L_2$ equilibrium, obtained from Fig 1, is 0 082° per bar which is close to the values, $(\partial t/\partial p)_d$, for the pure solvent, H_2O One experimental run each, made with a 2 758 molal stoicheiometric UO_2F_2 solution and with a 1 306 molal $CuSO_4$ solution containing 0 242 molal H_2SO_4, both of which exhibit liquid–liquid immiscibility near 320°, gave values of $(\partial t/\partial p)_x$ of ~0 10 and ~0 11, respectively, for the change in immiscibility temperature with pressure (Fig 2) The corresponding values, $(\partial t/\partial p)_d$, for H_2O, at the temperature of appearance of 2L in the presence of V for each system, were 0 105 and 0 112, respectively An assumption is made that $(\partial t/\partial p)_d$ for the various solutions at pressures at least up to 300 bars is nearly the same as that for the solvent H_2O (although their respective densities will vary with concentration) With this assumption it appears that the temperature of liquid-liquid immiscibility for the several salt solutions, in particular for stoichiometric UO_2SO_4 solutions at temperatures near 300 , is, to a first order, dependent on density If isobaric plots of density versus temperature are made for a particular liquid-phase composition (L) then the second-liquid-phase should first appear when the density decreases to a unique value for all isobars The fact that $(\partial t/\partial p)_x$ for solutions of high concentration is still approximately the same as $(\partial t/\partial p)_d$ for H_2O, independent of the phase which separates or the above assumption, seems to indicate a first order dependency on *solvent* density or on another property, particularly dielectric constant, which is strongly dependent on density

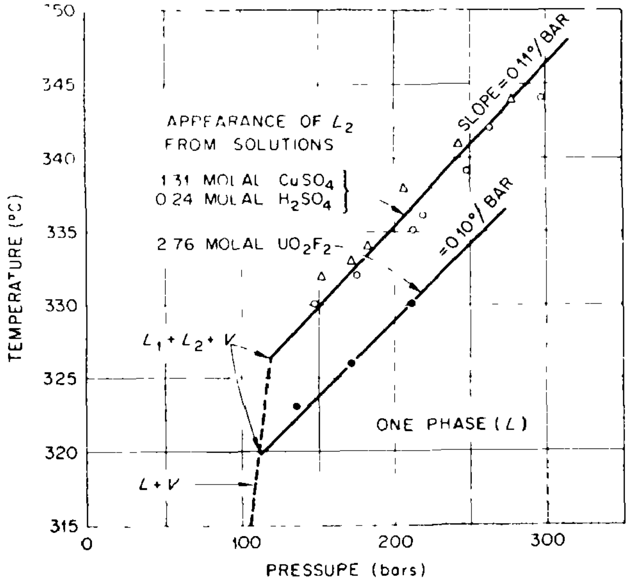


FIG 2 —Effect of pressure on the temperature of liquid-liquid immiscibility for one H_2O solution of UO_2F_2 and one of $CuSO_4$ and H_2SO_4

The data in Table 1 were used to make diagrams of pressure and composition showing two-liquid phase boundaries for stoicheiometric UO_2SO_4 solutions at constant temperature An example of these showing the relationships at 310° is given in Fig 3 *The points in Fig 3 were read off the curve of Fig 1, or from an extrapolated portion,* and were converted to actual values of pressure and temperature Since in each of the two liquid phases R_L, defined as m_{UO_3} m_{SO_3}, usually is not unity,[2] Fig 3 in reality is a plane showing compositional boundaries at $R_L = 1$ 0 of the three-component system UO_3 SO_3–H_2O, the tie lines of which are undefined

---

[6] W T HOLSER and G C KENNEDY, *Amer J Sci* **256**, 744–53 (1958)

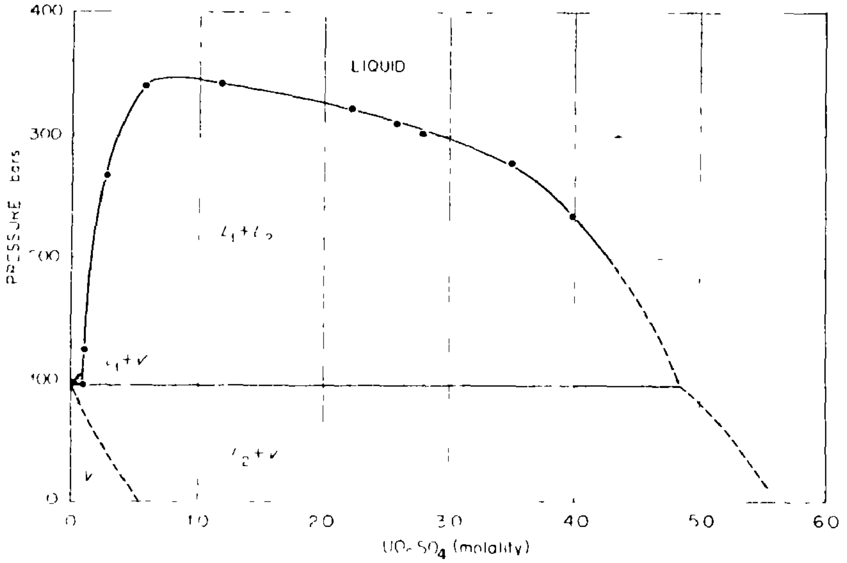


FIG 3 —The two liquid phase boundary for stoichiometric UO_2SO_4 solutions at 310 C

Effect of pressure on liquid-supercritical fluid equilibria in the system UO_3–SO_3–H_2O

The temperature of immiscibility can be raised by the addition of H_2SO_4 to stoichiometric UO_2SO_4 solutions [7] If the system is now designated in terms of the components, UO_3, SO_3, and H_2O, and sufficient H_2SO_4 is added to lower the molal ratio, R_L, below about 0 35, then the critical temperature (where $L = V$) of L is reached before the appearance of a second-liquid phase This liquid phase may separate from the supercritical fluid (F1) at temperatures above the critical temperature, and the temperature is a multiple function of the composition of the system and the pressure

The results of several runs on solutions containing UO_3, SO_3, and H_2O which had values of R_L of less than 0 35 are shown in Fig 4 In some experiments not only were the pressure–temperature relationships of the equilibria, $L_2 + F1$, established but also bubble points, where vapour is produced from liquid phase upon lowering the pressure on the system These bubble points thus correspond closely to the vapour-pressure curve which extends to the critical temperature and pressure for the particular composition of the condensed system At higher temperatures the supercritical fluid exists from which, upon lowering its pressure, L_2 appears

The values, $(\partial t/\partial p)_{a}$, for pure H_2O at the lowest pressure and temperature of

---

(7) W L MARSHALL, E V JONES, G M HEBERT and F J SMITH, *J Inorg Nucl Chem*, **24**, 995 (1962)

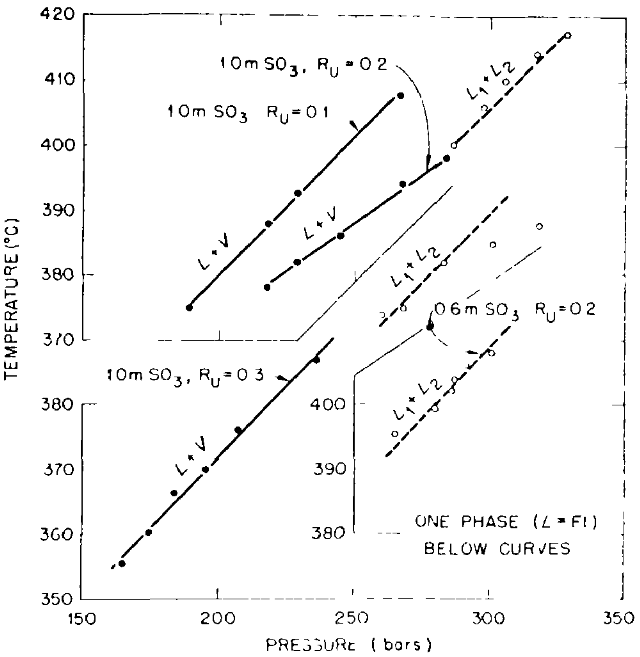


FIG 4 —Effect of pressure on the temperature of liquid-liquid immiscibility for solutions of UO_3, SO_3, and D_2O ($R_U = m_{UO_3}/m_{SO_3}$)

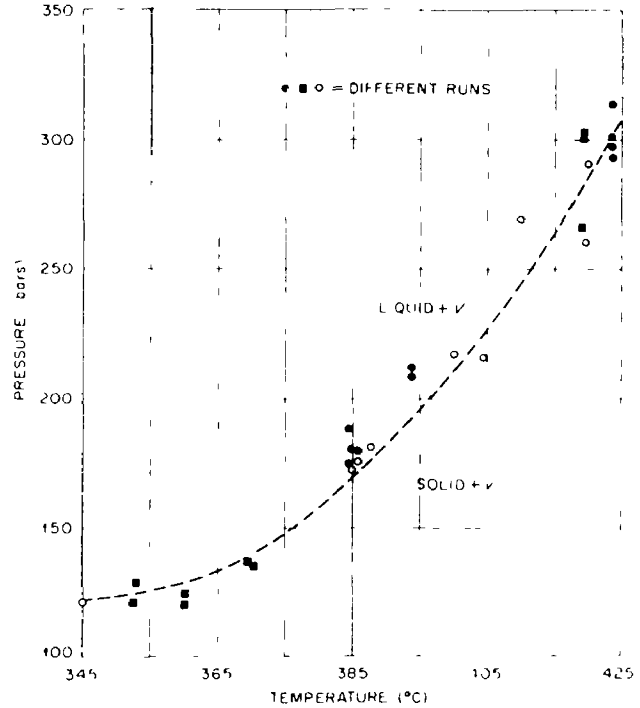


FIG 5 —The vapour-pressure of deliquescence of UO_2SO_4 hydrate solid 345-425 C

observation of L_2 were used to draw the dashed lines in Fig. 4 and are approximately the same magnitude as those of $(\partial t/\partial p)_\rho$ for the P–T curve for L_2-Fl. Therefore at temperatures near 400°, as was observed for the formation of a second-liquid phase near 300°, the boundary limit of liquid phase formation from supercritical fluid appears to show a first order dependency on density of the solvent.

These visual observations further substantiated the high concentrations of UO_3 found previously in supercritical SO_3-H_2O fluids. It appears that moderately low pressures (of the order of 300–600 bars) would extend the T–P boundaries of liquid phase in contact with supercritical fluid to temperatures over 500° for aqueous fluids of at least 0.2–0.3 molal in UO_3 and 1.0 molal in SO_3.

Vapour-pressures of deliquescence of solid UO_2SO_4 *hydrate*

By making use of the visual method some vapour-pressures at which solid UO_2SO_4 hydrate deliquesced were determined. The data of several runs are shown in Fig. 5, and are believed to scatter because of the difficulty in observing the start of dissolution to form a liquid upon increasing the water pressure and the appearance of supersaturation upon decreasing the pressure. This curve describes the pressure-temperature relationships in accordance with which three phases, gas, liquid and solid are in equilibrium, originating from the system UO_2SO_4–H_2O. However, the equilibrium compositions of the three phases may contain excesses or deficiencies of acid.

Note added in proof. By means of a new optical cell, recently developed at this Laboratory, the effects of pressure on liquid-liquid immiscibility in the system UO_2SO_4–H_2O have been extended to 1700 bars at temperatures up to 400°. The curves given in Fig. 1 extend linearly to the highest pressure with an average revised value of the slope, $\Delta t/\Delta p$, of +0.075°/bar for UO_2SO_4 solutions from 0.28 to 4.53 molal. From E. U. FRANCK's estimates of the dielectric constants (D) of water [*Z. phys. Chem.* (Frankfurt) **8**, 107 (1956)], the value, $(\partial t/\partial p)$, at constant DT (°K) at the L–V point of H_2O is estimated to be +0.075°/bar at 290° and +0.079°/bar at 300°. Thus liquid–liquid immiscibility appears to correlate well with a function of theoretical significance, the product of the dielectric constant of the solvent times the absolute temperature. Details of the cell and experimental results are to be published soon.

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 1041 to 1044. Pergamon Press Ltd. Printed in Northern Ireland

THE SOLUBILITY OF INDIUM HYDROXIDE IN ACIDIC AND BASIC MEDIA AT 25°C

L. C. A. THOMPSON and R. PACER
University of Toledo, Toledo 6, Ohio

(*Received* 20 *December* 1962, *in revised form* 1 *February* 1963)

Abstract—The solubility of $In(OH)_3$ was measured in NaOH and $HClO_4$ solutions. Possible reactions of $In(OH)_3$ in dilute NaOH and $HClO_4$ are indicated along with the calculated constants. The result indicated conclusively that $In(OH)_3$ is only slightly amphoteric, being much more basic than acidic.

THE amphoteric nature of indium hydroxide has been studied by other investigators from both a theoretical and an experimental approach. A comparison of the results of these works shows no close agreement as to the extent of this property. SUN[1] used a formula which takes into consideration the atomic number, valence and principal quantum number and concluded that indium hydroxide was basic and not amphoteric. LUI[2] calculated the electronegativity of several elements and related it to amphoteric character. Applying this to indium one again concludes that the oxide of indium is non amphoteric, functioning only as a base. However, IVANOV-EMIN[3] made a study of scandium, gallium and indium to determine the amphoteric properties of the hydrates of their oxides and found that all three exhibited amphoteric properties. DICHMAN[3] on the other hand, in a study of the system $InCl_3$–NaOH–H_2O did not observe the formation of soluble or insoluble indates. MOELLER[5] also did not observe the formation of indate solutions in his work. KLEINBERG[6] reported that In_2O_3 is primarily basic, being readily soluble in acids and slightly soluble in strongly alkaline solutions. EPHRAIM[7] related the reprecipitation of $In(OH)_3$ in excess strong base to a change in its colloidal nature upon standing in such a solution.

EXPERIMENTAL

Procedure

The general procedure is similar to that of GARRETT and HEIKS[8].

Preparation of reagents

Water. High purity water was prepared by boiling deionized water and then storing under nitrogen.

Sodium hydroxide. Approximately 1.5 molar solutions of base were prepared under nitrogen by dissolving Baker and Adamson reagent pellets with boiled and cooled deionized water. The solutions were also prepared and standardized with 0.1000 N HCl.

Perchloric acid. Approximately 0.3 molar solutions of acid were prepared from 72 per cent $HClO_4$. Standard solutions were also prepared.

---

[1] C. SUN and S. LI, *J. Chinese Chem. Soc.* **7**, 69–72 (1940).

[2] I. LUI, *J. Chinese Chem. Soc.* **9**, 119–24 (1942).

[3] B. IVANOV-EMIN, Sbornik Nauch. Troduv Moskov Inst. Tsvetnoi Met. i Zalota No. **27**, 7–22.

[4] E. DICHMAN, E., Akad. Nauk. SSSR *Inst. Obsh. Neorg.* Khim. No. **3**, 73–86 (1957).

[5] T. MOELLER, *J. Amer. Chem. Soc.* **63**, 1026–7 (1941).

[6] J. KLEINBERG, *Inorganic Chemistry*, Heath, Boston (1960).

[7] F. EPHRAIM, *Inorganic Chemistry* (6th Ed.) Interscience, New York (1954).

[8] A. GARRETT and R. HEIKS, *J. Amer. Chem. Soc.* **63**, 562 (1941).

Indium chloride Anhydrous indium chloride from the Indium Corporation of America was used to prepare 1 M solutions Standard indium solutions were also prepared and checked against standard EDTA

EDTA Solutions of 0 0100 molar ethylene diamine tetraacetic acid were prepared by weighing 3 7225 g of the Eastman Kodak disodium salt Solutions of lesser concentrations were prepared from aliquots of this stock solution

1-(2-pyridylazo)-2-Naphthol Indicator An indicator solution of 0 1 per cent strength was prepared by dissolving 10 mg of this indicator in 10 ml of methanol

Measurement of pH

The reaction flasks were broken while enclosed in a rubber membrane and samples were withdrawn using a hypodermic needle An Analytical Model 700 pH meter was used after standardization at pH 9 for the basic series of samples and again at pH 4 for the acid series of samples

Determination of In^{3+}

CHENG(9) reported that indium could be determined volumetrically with EDTA Titration of standard solutions of $InCl_3$ against EDTA using 1-(2-pyridylazo)-2-naphthol indicator yielded good results The colour change is very sharp going from red to pure yellow

THE DATA

The solubility data are collected in Tables 1 and 2 The values for the activity coefficients for NaOH and $HClO_4$ are given by ROBINSON and STOKES(10)

TABLE 1 SOLUBILITY OF INDIUM HYDROXIDE IN SODIUM HYDROXIDE SOLUTIONS AT 25 C

Initial NaOH/100 g H_2O 10^2 (M)	$In(OH)_3$/1000 g H_2O 10^3 in solution at Equilibrium (M)	K_1 10^1	K_2 10^2	K_3 10^2
0 76	0 70	9 2	7 70	77 0
4 80	5 70	11 9	1 68	30 6
7 09	6 75	9 5	0 86	9 4
6 46	6 35	9 8	0 98	12 1
6 03	5 65	9 4	1 01	13 9
		Ave K_1 1 0 10^{-3}	Ave K_2 2 4 10^{-2}	Ave K_3 2 9 10^{-1}
			σ - 2 7 10^{-2}	σ 2 5 10^{-1}

TABLE 2 -SOLUBILITY OF INDIUM HYDROXIDE IN PERCHLORIC ACID SOLUTIONS AT 25 C

Initial $HClO_4$/1000 g H_2O 10^3 (M)	$In(OH)_3$/1000 g H_2O 10^3 in solution at Equilibrium (M)	K_4	K_5 10^{-2}	K_6 10^{-1}
1 07	1 92	1 79	16 4	164 0
1 58	2 07	1 31	8 0	53 0
5 89	10 30	1 75	2 7	4 1
6 30	9 45	1 50	2 1	3 0
7 07	9 90	1 40	1 8	2 2
		Ave K_4 1 6		

---

(9) K CHENG, *Analyt Chem* **27,** No 10, 1582–3 (1955)

(10) R ROBINSON and R STOKES, *Trans Faraday Soc* **45,** 612 24 (1949)

The equilibrium constants given are for the following reactions:

$$In(OH)_3(S) + OH^- = H_2InO_3^- + H_2O \qquad (1)$$

$$In(OH)_3(S) + 2OH^- = HInO_3^{2-} + 2H_2O \qquad (2)$$

$$In(OH)_3(S) + 3OH^- = InO_3^{3-} + 3H_2O \qquad (3)$$

In view of the constancy of K_1 when compared with K_2 and K_3, it is felt that Equation (1) represents the predominant reaction of $In(OH)_3$ in basic solutions up to about 0.07 molal.

$$K_1 = \frac{M_{H_2InO_3^-}\,\gamma_{H_2InO_3}}{M_{OH}\,\gamma_{OH^-}}$$

According to the Debye–Huckel limiting law, the activity coefficients for 1:1 electrolytes should be equal at equal ionic strengths, hence

$$\gamma_{H_2InO_3^-} = \gamma_{OH^-} = \gamma'_{NaOH}$$

and

$$K_1 = \frac{M_{H_2InO_3^-}}{M_{OH}} = 1.0 \times 10^{-3}$$

$$\Delta F_1^\circ = -RT \ln K_1 = 4100 \text{ cal/mole.}$$

$$K_2 = \frac{M_{HInO_3^{2}}\,\gamma_{HInO_3^{2}}}{a^2_{OH^-}}$$

From the Debye–Huckel limiting law, the activity coefficient of a 1:2 electrolyte may be replaced by the square of that for a 1:1 electrolyte, hence

$$K_2 = \frac{M_{HInO_3^{2-}} \cdot \gamma'^2_{HInO_3^{2-}}}{a^2_{OH^-}} = 2.4 \times 10^{-2}$$

In the same manner applying the Debye–Huckel law to a 1:3 electrolyte

$$K_3 = \frac{M_{InO_3^{3}}\,\gamma'^3_{NaOH}}{a^3_{OH}} = 2.9 \times 10^{-1}$$

The equilibrium constant K_4 is for the following reaction and is evaluated as shown below

$$In(OH)_3(S) + H^+ = In(OH)_2^+ + H_2O \qquad (4)$$

$$K_4 = \frac{a_{In(OH)_2^+}}{a_{H^+}} = \frac{M_{In(OH)_2^+} \cdot \gamma'_{In(OH)_2^+}}{a_{H}}$$

as before

$$\gamma_{In(OH)_2^+} = \gamma'_{HClO_4}$$

and

$$K_4 = \frac{M_{In(OH)_2^+}\,\gamma_{HClO_4}}{a_{H^+}}$$

$$\Delta F_1^\circ = 280 \text{ cal/mole}$$

K_5 and K_6 were calculated for the following reactions

$$In(OH)_3 + 2H^+ = In(OH)^{2+} + 2H_2O \qquad (5)$$

$$In(OH)_3 + 3H^+ = In^{3+} + 3H_2O \qquad (6)$$

using the following expressions

$$K'_5 = \frac{M_{In(OH)_2^+} \gamma^2_{HClO_4}}{a^2_{H^+}}$$

and

$$K'_6 = \frac{M_{In^{3+}} \gamma^3_{HClO_4}}{a^3_{H^+}}$$

In view of the trend in K'_5 and K'_6 as noted in Table 2 no attempt was made to determine the extent to which the reactions occurred. However, from the constancy of K'_4 it can be concluded that the predominant reaction taking place in acid media at the concentration-range studied is reaction (4).

CONCLUSION

From the above data we can conclude that $In(OH)_3$ is much more soluble in acid than in base thus showing that it is more basic than acidic. The reactions that are most likely taking place in the concentration ranges studied are for the basic equilibria,

$$In(OH)_3(S) + OH^- \rightleftharpoons H_2InO_3^- + H_2O$$

and for the acidic equilibria

$$In(OH)_3(S) + H^+ \rightleftharpoons In(OH)_2^+ + H_2O$$

Acknowledgement—The authors gratefully wish to acknowledge the gift of the indium chloride used in this work from the Indium Corporation of America.

J Inorg Nucl Chem 1963 Vol 25, pp 1045 to 1050 Pergamon Press Ltd Printed in Northern Ireland

SEPARATION OF RARE EARTHS BY MEANS OF SMALL COLUMNS OF KEL-F SUPPORTING DI(2-ETHYLHEXYL)ORTHOPHOSPHORIC ACID

E Cerrai and C Testa
Laboratori CISE Segrate (Milano)*

(*Received* 5 *November* 1962, *in revised form* 21 *January* 1963)

Abstract—The tracer level separation of rare earth elements has been achieved by using a small column (3 mm i d 140 mm height) of Kel-F powder (polytrichlorofluoroethylene) loaded with di(2-ethylhexyl)orthophosphoric acid (HDEHP) Suitable column preparation procedure has been determined by investigating the Eu-Tb separation The column was operated at 85 ± 1 C and elution was carried out with a solution of hydrochloric acid having the proper concentration For the resolution of mixtures containing more than two lanthanide elements the gradient elution method was used

The following separations are reported Eu-Tb, Eu-Gd-Tb-Sm, La-Ce-Pr-Nd-Pm-Sm-Eu, La-Pr-Sm-Eu-Gd-Tb-Dy-Ho-Er-Tm-Yb-Lu, Tb-Yb

Reversed phase partition chromatography has received attention for the separation of rare earths on columns supporting phosphate esters such as tri-n-butylphosphate(1,2) and di(2-ethylhexyl)orthophosphoric acid(3–8) In fact, liquid–liquid extraction of rare earths by means of such organic substances presents an average separation factor for a pair of adjacent lanthanides of about 2 0 in the case of TBP(9) and of 2 5 in that of HDEHP (10)

Besides simple paper sheets used for reversed phase chromatography of rare earth elements,(11) many different porous materials have been used to support the organic phase in column techniques They are cellulose powder,(6,7) kieselghur,(1,2) alumina or polystyrene divinylbenzene(3,4) and poly(vinylchloride-vinylacetate) (5,8) Since polytrifluorochloroethylene (Kel-F) had been shown to be a very suitable support(12,13) for various organic substances, we investigated its applicability to the tracer level separation of the whole rare-earth group by means of a small column containing HDEHP Each individual rare earth element was obtained in a fraction of eluate having a volume smaller than 1 ml

---

* Address CISE Casella Postale 3986 Milano ITALY

(1) S Siekierski and I Fidelis, *J Chromatogr* **4**, 60 (1960)

(2) I Fidelis and S Siekierski, *J Chromatogr* **5**, 161 (1961)

(3) J W Winchester, ORNL-CF-58 12-43 (1958)

(4) J W Winchester ORNL CF-60-3 158 (1960)

(5) T B Pierce and P F Peck *Nature, Lond* **194**, 84 (1962)

(6) E Cerrai, C Testa and C Triulzi, *Energia Nucleare* (Milan) **9**, 193 (1962)

(7) E Cerrai, C Testa and C Triulzi, *Energia Nucleare* (Milan) **9**, 377 (1962)

(8) T B Pierce and P F Peck, *Nature Lond* **195**, 596 (1962)

(9) D F Peppard, W J Driscoll, R J Sironen and S McCarty, *J Inorg Nucl Chem* **4**, 326 (1957)

(10) D F Peppard, W J Driscoll, R J Sironen and S McCarty, *J Inorg Nucl Chem* **4**, 334 (1957)

(11) E Cerrai and C Testa, *J Chromatogr* **8**, 232 (1962)

(12) A G Hamlin, B J Roberts, W Loughlin and S G Walker *Analyt Chem* **33**, 1547 (1961)

(13) E Cerrai and C Testa, *J Chromatogr* **9**, 216 (1962)

EXPERIMENTAL

Reagents and equipment

Di(2-ethylhexyl)orthophosphoric acid, the composition of which is $(CH_3—(CH_2)_3—CH—(C_2H_5)—CH_2O)_2POOH$, had been supplied by Soc Eigenmann and Veronelli (Milano), and Kel-F low density powder, grade 300, by Minnesota S p A (Milano) Before use, Kel-F was ground in a laboratory mill and sieved to 170-230 mesh

Natural rare earths were obtained from Light's (London England) and Fluka (Buchs S G Switzerland) A few milligrams of each element in a group of eleven rare earths were sealed in different

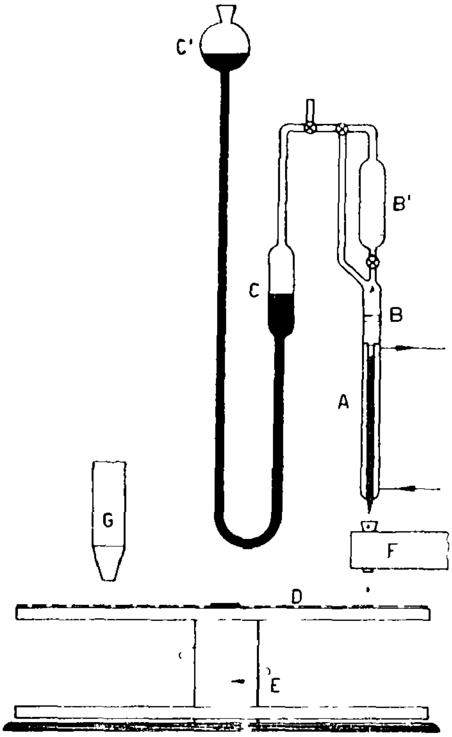


FIG 1 -Diagrammatic sketch of the apparatus used for column separation of rare earth elements *A* jacketed column kept at a constant temperature *B* lower container of the gradient elution system, *B'* higher container of the gradient elution system, *C* and *C'* mercury containing bulbs, *D* paper disk, *E* rotating fraction collector, *F* photocell device for elution control, *G* warm air blower

quartz ampoules and irradiated for about a week in the core of the Avogadro I swimming pool reactor of SORIN (Saluggia) An integrated neutron flux (thermal) was reached of about 8 10^{18} n/cm^2 After irradiation, the following radionuclides were obtained and used for the separation experiments at a tracer level (40hr)^{140}La, (32 5 day)^{141}Ce, (33 hr)^{143}Ce, (19 hr)^{142}Pr, (13 8 day)^{143}Pr, (11 3 day)^{147}Nd, (27 hr)^{151}Pm*, (47 hr)^{153}Sm, (2 42 hr)^{165}Dy, (27 3 hr)^{166}Ho, (9 4 day)^{169}Er, (7 5 hr)^{171}Er, (31 8 day)^{169}Yb, (4 2 day)^{175}Yb, (3 75 hr)^{176}Lu, (6 7 day)^{177}Lu To complete the rare earth group, $^{152+154}$Eu, ^{153}Gd, ^{160}Tb and ^{170}Tm were obtained from the Radiochemical Centre (Amersham, England)

All the other reagents were analytical grade

The electronic automatic fraction collector Paris-Labo (Paris-France) type TFC was used

A diagram of the apparatus used for elution and fraction collection is shown in Fig 1 The Pyrex column *A* (3 mm i d) was fitted with a glass jacket into which a constant temperature water (±1°C) flow was circulated from a laboratory water-bath Containers *B* and *B'* form the gradient elution system and mercury bulbs C and C' the pressurizing device. A large paper disc D, cut away from a Whatman no. 3 sheet, and previously spread with an alcoholic solution of xylenol orange, was fixed onto the rotating plate of the fraction collector E. Every drop (about 0.012 ml) of eluate which passed through the photocell device F made the plate switch to the nearest position. In this way, up to about 200 drops could be separately collected on a paper disk. Drops were dried during operation with a warm air flow from the electrical blower G.

---

* From the parent (15 min) ^{151}Nd

Since the eluate was acidic because of the presence of HCl in the eluent, the positions of drops on the paper disc were clearly revealed by an orange spot due to the reaction of xylenol orange which had been previously fixed to the paper. When a disc was complete, paper was removed from the rotating plate, and spots were covered with a slip of a 5 cm wide "Scotch" adhesive tape applied on both sides of the paper. Spots were numbered and cut away from the disc. Each portion, which was formed by a spot within a "Scotch" tape sandwich, was γ-counted with a 1½ × 1½ in. NaI(Tl) scintillation crystal mounted on a photomultiplier tube and fitted with the pertinent electronic equipment. The various radionuclides were identified by γ-spectroscopy that was carried out on spots corresponding to elution peaks. Gamma spectroscopy was performed by means of the above mentioned scintillation system, completed with a 256-channel magnetic-memory pulse-height analyser (CISF type D 2100) fitted with an automatic IBM printing machine.

Effect of the preparation procedure on column separation of Eu-Tb

Before studying the separation of a group of rare earth elements, the effect of the preparation procedure on the column performance was investigated. Eu and Tb were selected as two intermediate weight rare earths and the following general procedure was used: a weighed amount of 170–230 mesh Kel-F powder (0.8 g) was mixed in a small beaker to 0.6 ml of an organic solution of HDEHP. After accurate stirring, 20 ml of 1.5 M HCl were added and the mixture was allowed to digest. Floating particles were removed from the liquid surface, and the material was transferred into the 3 mm i.d. column by using a thin glass rod. The bed was then gently pressed to eliminate air bubbles and a 140 mm height resulted. The column was conditioned with 15 to 20 ml of 1.5 M HCl, and then 0.02 ml of 1.5 M HCl containing Eu and Tb were fed onto the bed. Thereafter elution was started with 0.05 ml/min (four drops/min) of 1.5 M HCl at room temperature (22 ± 1 °C). Single drops were collected during elution as described above and afterward counted in groups of three. Peak and valley for each element were determined by separately measuring each drop.

Five slightly different preparations have been considered.

(a) Kel-F powder and undiluted HDEHP were directly mixed and stirred. Then the column was prepared as described above. This column has a high capacity but the two peaks appear rather large and flattened. An eluate volume of 800 drops was required, Eu having the maximum at 70 and Tb at 410.

(b) Kel-F powder was mixed to a solution of HDEHP/cyclohexane (1/2 vol) and column prepared. With an eluate volume of 400 drops peaks appeared narrower than in case (a), Eu and Tb maxima were 60 and 190 respectively.

(c) Kel-F powder was mixed to a solution of HDEHP/chloroform (1/2 vol). After intimate mixing chloroform was removed by heating at 50 °C for 1 hr. Results were very similar to those of case (b).

(d) Kel-F powder was mixed to a solution of HDEHP/cyclohexane (1/7.5 vol). The peaks were very narrow and both in about 200 drops of eluate, Eu and Tb maxima occurred at 60 and 95 respectively.

(e) Kel-F was mixed to a solution of HDEHP/chloroform (1/7.5 vol). The solvent was eliminated by heating at 50 °C for 1 hr. Peaks appeared very narrow (at 60 and 110 respectively) and a higher peak to valley ratio was obtained.

As repeatedly verified in our laboratory with several column experiments and in a systematic study(11) on the paper chromatography of rare earth elements on strips treated with HDEHP and eluted with HCl, the position of the elution peak for a given element, beyond the interstitial volume of the column, (or R_F value in paper chromatography) is a function of the acidity of the eluting phase. The lower the acidity the more delayed the peak or lower the R_F. Furthermore, under fixed conditions the higher the atomic number of the element the more delayed the peak (lower R_F). In fact the same trend was shown by the Eu-Tb pair when the column prepared as in (e) was eluted with 1 M HCl instead of 1.5 M, peaks appeared delayed and more apart, i.e. at 95 and 390 respectively.

On the basis of the results described above, it was decided to use the standard column with the preparation (c) for the separation of many rare earths from one another

SEPARATION OF RARE EARTHS

Some preliminary experiments were carried out on rare earth groups which were known to present some difficulties Amongst them the group formed by Sm-Eu-Gd Tb will be briefly considered here It was realized at once that the favourable effect of temperature on the separation of adjacent pairs[7] had to be exploited to get satisfactory results In addition, the use of a constant acidity eluent did not allow a complete separation mainly of the closest pair Eu Gd, which normally in HDEHP columns exhibits a separation factor substantially lower than the average value (1 65 vs 2 50)

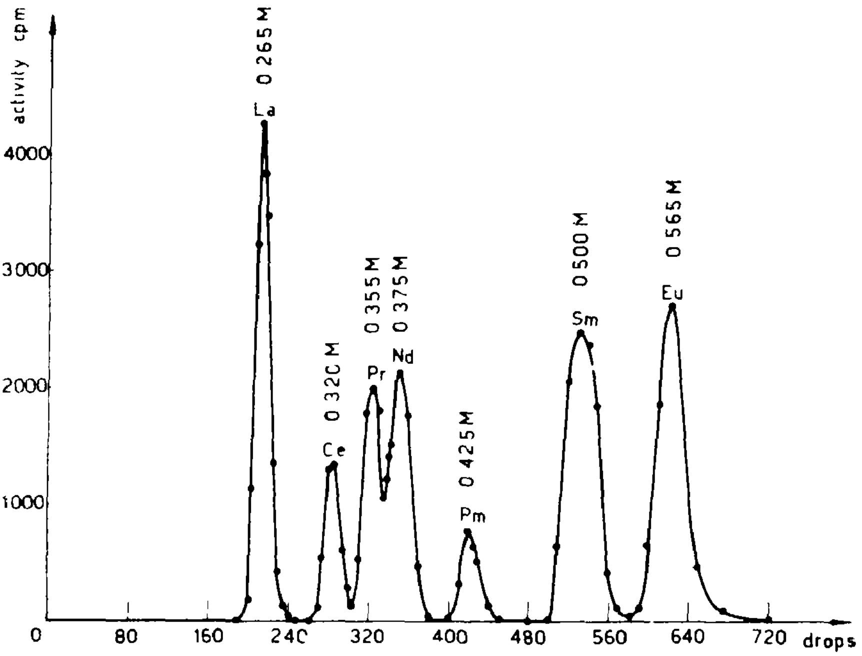


FIG 2 – Separation of La-Ce-Pr-Nd Pm-Sm-Eu at 85 ± 1°C Feed solution 0 04 ml of a solution containing the elements at a tracer level Gradient elution with HCl, the molarity is quoted in the plot Flow-rate 0 025 ml/min (2 drops/min)

The separation of the four components succeeded in 5½ hr by operating with a gradient elution at 2 drops/min and at 85 ± 1°C, the feed solution being 0 02 ml in volume and 0 4M in HCl The gradient elution was carried out by means of the two containers *B* and *B′* of Fig 1 The lower container *B* was filled with 15 ml of 0 4 M HCl and *B′* with 1 2M HCl Each drop of eluate that left the column was compensated by a drop that passed from *B′* to *B* Owing to the strong convective mixing of liquid in *B*, due to the temperature gradient, the effect of each 1 2 M HCl drop was to increase immediately the concentration of the acid Therefore an eluent having a gradually increasing concentration of HCl flowed through the column

Since obviously the gradient elution method is very useful when several components have to be separated, it was used by us in all the separations of more than two lanthanides which are described in the following

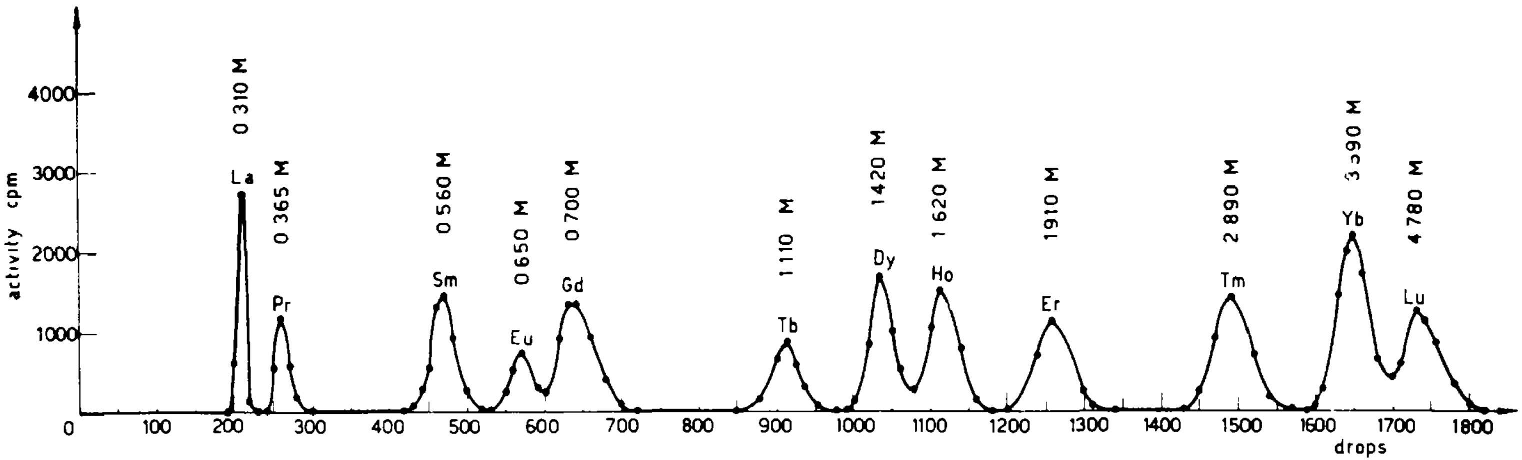


FIG. 3 —Separation of La-Pr-Sm-Lu-Gd-Tb-Dy-Ho-Er-Tm-Yb-Lu at 85 1 C Feed solution 0 04 ml of a solution containing the elements at a tracer level Gradient elution with HCl, the molarity is quoted in the plot Flow-rate 0 06 ml min (4 8 drops/min)

The series of the first seven rare earth elements (La–Ce–Pr–Nd–Pm–Sm–Eu) was then considered and separation carried out with the same technique described above. The feed solution (0.02 ml) was prepared in 0.1 M hydrochloric acid. After adsorption on the column, gradient elution was started with 0.1 M HCl (15 ml) in the lower container B and 1.2 M HCl in *B′* at a flow-rate of 2 drops/min. The column was kept at 85 ± 1°C. The elution plot is shown in Fig. 2. The separation obtained is satisfactory except for some overlap of Pr and Nd peaks. Such an overlap has been recorded also by other authors. The time required for the whole separation was 5½ hr with a total volume of eluate of 10 ml. Each component was contained in a total volume of 1 ml or less.

The best operating conditions were established for the separation of the complete group of the rare earth elements. Amongst the lighter elements of the group only La, Pr, Sm and Eu were considered, since the group of the first seven lanthanides had been already resolved (see Fig. 2). All the remaining rare earths from Gd to Lu were considered. A 0.1 M HCl solution containing the twelve components (La–Pr–Sm–Eu–Gd–Tb–Dy–Ho–Er–Tm–Yb–Lu) was prepared and a volume of 0.04 ml fed onto the column. Gradient elution at 4.8 drops/min was carried out at 85 ± 1°C. The initial acidity conditions in the gradient elution device were 15 ml of 0.1 M HCl in *B* and 1.5 M HCl in *B′*. After the break-through of Gd the 1.5 M HCl in *B′* was replaced with 4 M HCl. After the erbium breakthrough the acid was again replaced with 12 M HCl. In this way the whole separation was obtained in about 6½ hr. As shown in Fig. 3 the separation of the twelve components is satisfactory and only three pairs are slightly less resolved. In fact a small overlap occurs for Eu–Gd, for Dy–Ho and Yb–Lu. In the right hand portion of the plot in Fig. 3 Tm and Yb appear sufficiently apart. Incidentally it should be noted that in a separate experiment on this pair alone the separation of Tm–Tb was achieved simply by eluting with 3.5 M HCl.

We conclude that small chromatographic columns based on Kel-F powder supporting are capable of separating practically each of the components of the rare earth element family. Since the lowest possible molarity of HCl for the elution of a lanthanide element is higher the higher the atomic number of the element, a gradient elution with hydrochloric acid from 0.1 M to 5 M resulted in the satisfactory resolution for all the rare earth elements at a tracer level.

J Inorg Nucl Chem, 1963, Vol 25, pp 1051 to 1063 Pergamon Press Ltd Printed in Northern Ireland

SOME ASPECTS OF SYNERGISM IN SOLVENT EXTRACTION—II*

SOME DI-, TRI- AND TETRAVALENT METAL IONS

M Zangen†

(*Received* 10 *July* 1962, *in revised form* 4 *September* 1962)

Abstract—Synergistic extraction of trivalent lanthanides and actinides, alkaline earths and thorium from hydrochloric solutions was studied, using a combination of a monoacidic phosphate or phosphonate ester (the chelating agent) with a neutral organophosphorus compound (the synergist) at varying concentrations in cyclohexane

Of the above, only lanthanides with $Z > 64$ and Ba failed to show any synergistic phenomena In general, the synergism was much less pronounced than in the case of U(VI)

The basic difference between synergism for U(VI) and for other ions is pointed out, formulae are proposed for the extracted species and the values of some equilibrium constants are derived

In a previous article(1) an attempt was made to determine the mechanism for synergistic extraction of U(VI) from acidic aqueous solutions into an organic phase consisting of a nonpolar diluent (benzene or cyclohexane) a monoacidic phosphate or phosphonate ester serving as chelating agent and a neutral organophosphorus compound (phosphonate or phosphine oxide) serving as synergist This work is an attempt to study the extraction of other metal ions in a similar system

Although Baes *et al*,(2) in their first report on synergism, disclaim the existence of this effect for almost any metal ion except U(VI), Healy,(3) and Irving and Edgington(4) have shown it to exist for the system TTA- neutral organophosphorus compound The increases in distribution ratio D reported by these authors are too high to be explained in terms of change in the dielectric constant, in analogy with the work of Goble and Maddock(5) The more so, since the distribution ratio is found to be higher in diluents of lower dielectric constant(6)

Since solvent extraction research is more and more using radioactive tracer techniques to determine the distribution ratio, the probability is increased that a solvent, even of high purity, will contain some other compound in amounts comparable to the extracted metal ion If this compound can take part in a mixed complex of the extracted ion, a synergistic effect may result which, unless detected and understood, would make the experimental data useless For this reason it is felt that any new knowledge on synergism may contribute to the study of solvent extraction in general

---

* Based on work performed under the auspices of the U S Atomic Energy Commission

† Israel Atomic Energy Commission Laboratories, Rehovot Israel at the time of this work Affiliate of the International Institute of Nuclear Science and Engineering, Argonne National Laboratory, Argonne, Illinois

(1) M Zangen, Part I, *J Inorg Nucl Chem* **25**, 581 (1963)

(2) C A Blake, C F Baes Jr, K B Brown, C F Coleman and J C White *The Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy Geneva* (1958) 15/P/1550 United Nations (1958)

(3) T V Healy, *J Inorg Nucl Chem* **19**, 314 (1961)

(4) H Irving and D D Edgington, *J Inorg Nucl Chem* **21**, 169 (1961)

(5) A G Goble and A G Maddock, *Trans Faraday Soc* **55** 591 (1959)

(6) T V Healy, *J Inorg Nucl Chem* **19**, 328 (1961)

EXPERIMENTAL

Source and mode of purification of the neutral synergists TOPO trioctylphosphine oxide, DB[BP] dibutyl butylphosphonate and DEH[EHP] di(2-ethylhexyl) 2-ethylhexylphosphonate were given in the preceding article (1)

The acidic chelating agents used in this work were HDOφP di[para(1,1,3,3-tetramethylbutyl)-phenyl]phosphoric acid HDEHP di(2-ethylhexyl)phosphoric acid, both as specified before,(1)

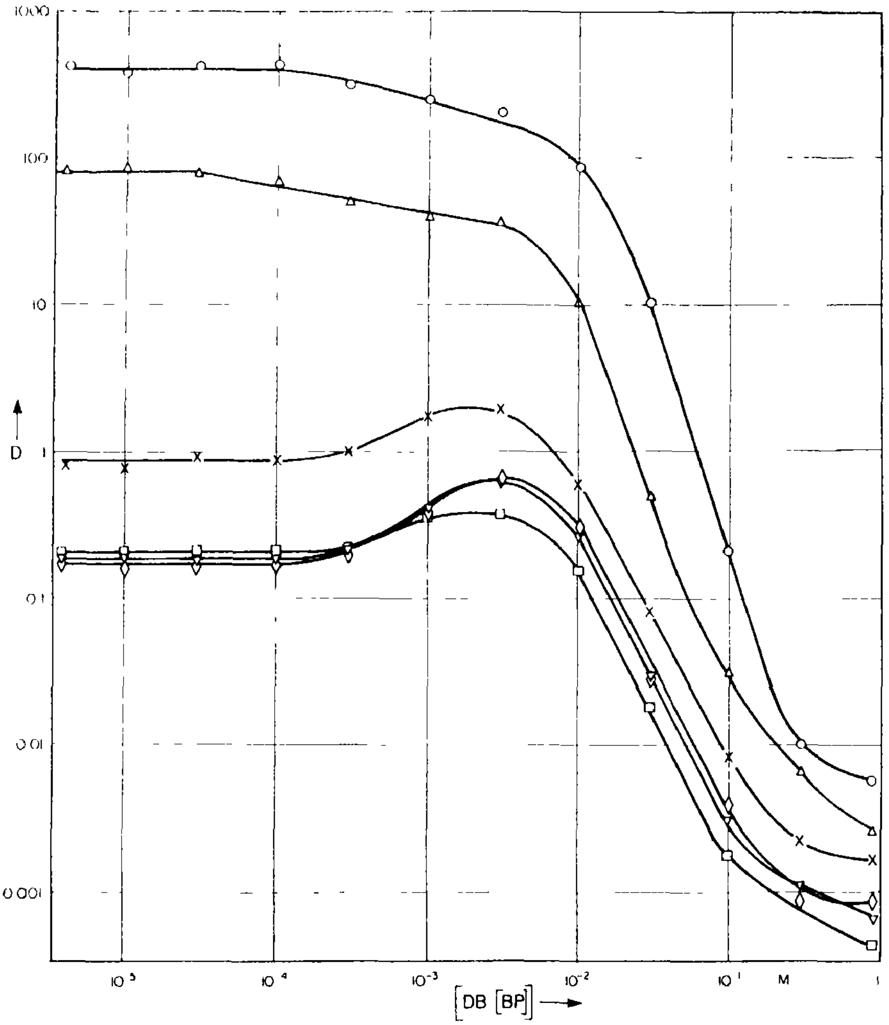


FIG 1 - Extraction of {○ Lu^{3+}, △ Tm^{3+}, × Eu^{3+}, □ Cm^{3+}, ▽ La^{3+}, ◇ Am^{3+}} from 0·3 N HCl by 3 × 10^{-3} F HDOφP in cyclohexane

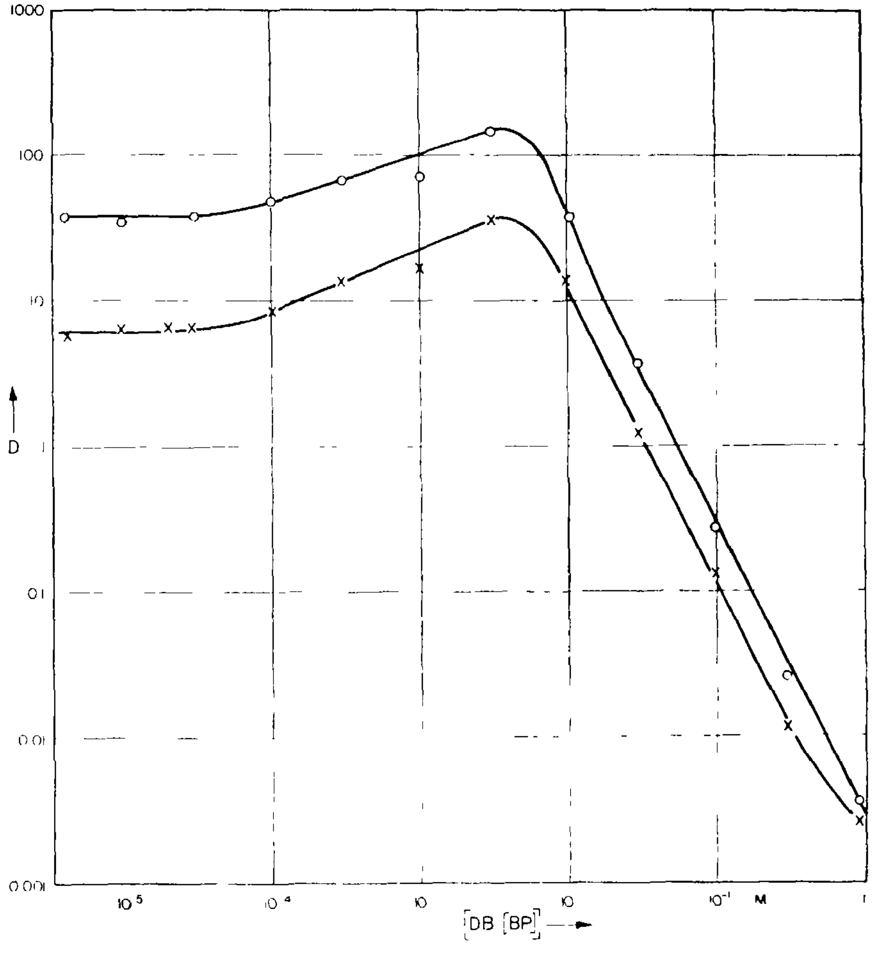


FIG. 2.—Extraction of $\left\{\begin{matrix} Eu^{III} \\ Am^{III} \end{matrix}\right\}$ from 0.3 N HCl by 10^{-2} HDOφP in cyclohexane

and HnO[φP] = n-octyl, hydrogen phenylphosphonate, obtained and purified according to the method of PEPPARD *et al*.(7)

The radioactive tracers used: ^{45}Ca(β^-, 164 day), ^{133}Ba(EC 9.5 year) ^{140}La(β^- 40 hr) ^{152}Eu(β^-, 13 year) + ^{154}Eu(β^-, 16 year), ^{160}Tb(β^- 73 day), ^{170}Tm(β^-, 129 day) ^{177}Lu(β^-, 6.8 day) ^{230}Th(α, 8 × 10^4 year), ^{241}Am(α, 470 year) and ^{244}Cm(α, 18 year) were obtained either from Argonne National Laboratory stocks or from the Isotope Division of Oak Ridge National Laboratory and purified by solvent extraction methods.

Determination of the distribution ratios was done radiometrically, as reported by PEPPARD *et al*.(8)

RESULTS

(*a*) *Extraction of* La(III), Eu(III), Tm(III), Lu(III), Am(III) *and* Cm(III) *from* 0.3 *N* HCl *by* 0.003 *F* HDOφP + *varying concentrations of* DB[BP] *in cyclohexane*

---

(7) D. F. PEPPARD, J. R. FERRARO and G. W. MASON, *J. Inorg. Nucl. Chem.* **12**, 60 (1959).

(8) D. F. PEPPARD, G. W. MASON, J. L. MAIER and W. J. DRISCOLL, *J. Inorg. Nucl. Chem.* **4**, 334 (1957).

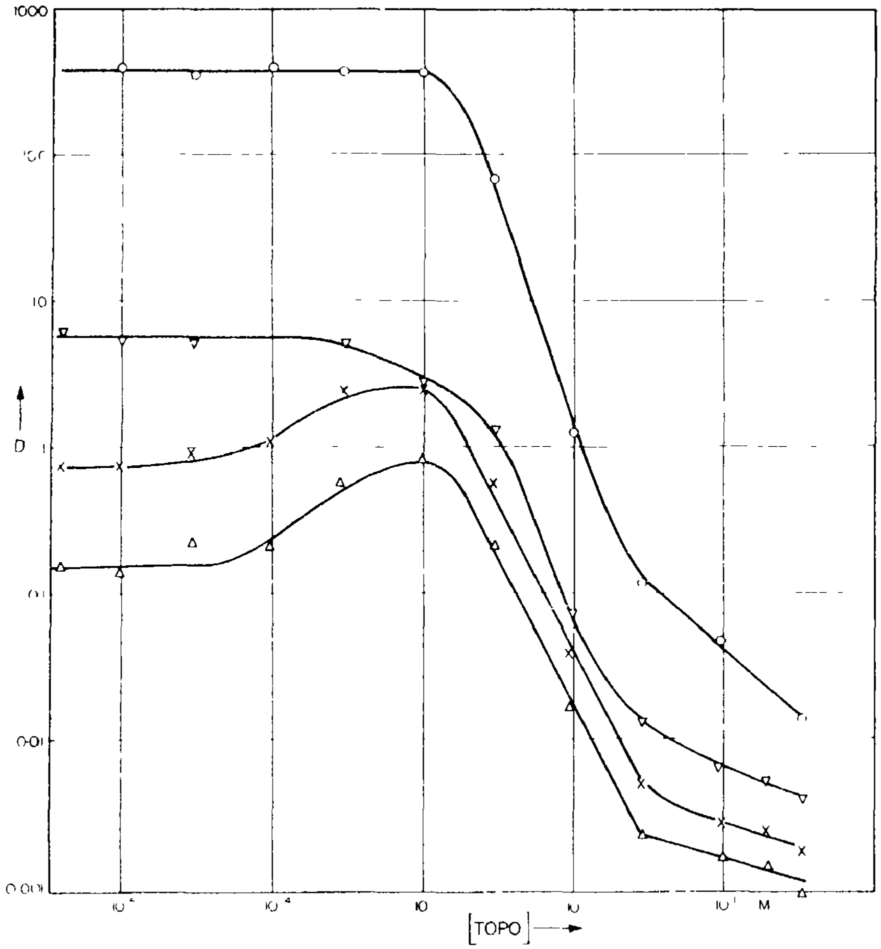


FIG. 3. Extraction of $\left\{\begin{array}{l} \circ\ \mathrm{Lu}^{3+} \\ \nabla\ \mathrm{Tb}^{3+} \\ \ \ \mathrm{Eu}^{3+} \\ \triangle\ \mathrm{Am}^{3+} \end{array}\right\}$ from 0·3 N HCl by 3×10^{-3} F HDOφP in cyclohexane

Results are shown in Fig. 1. At 0·002 M DB[BP], a maximum increase in D was found for La, Eu, Am and Cm, by factors of ~3·5, ~2·5, ~4 and ~2 respectively. No synergistic effect was found for Tm and Lu. The slope of the antisynergistic (decreasing) part of the D vs. [DB[BP]] plot (log-log scale) was appromixately −2 for La, Eu, Am and Cm, and near −3 for Tm and Lu.

(b) *Extraction of* Eu(III) *and* Am(III) *from* 0·3 *N* HCl *by* 0·01 *F* HDOφP + *varying concentrations of* DB[BP] *in cyclohexane.* Fig. 2 shows a maximum increase in D at 0·004 M DB[BP] for both Eu and Am, by factors of ~4 and ~6 respectively. The antisynergistic slope is again −2 for both metals.

(c) *Extraction of* Eu(III), Tb(III), Lu(III) *and* Am(III) *from* 0·3 *N* HCl *by* 0·003 *F* HDOφP + *varying concentrations of* TOPO *in cyclohexane.* Fig. 3 shows a maximum increase in D at 0·001 M TOPO for both Eu and Am, the factors being ~3·5 and ~5

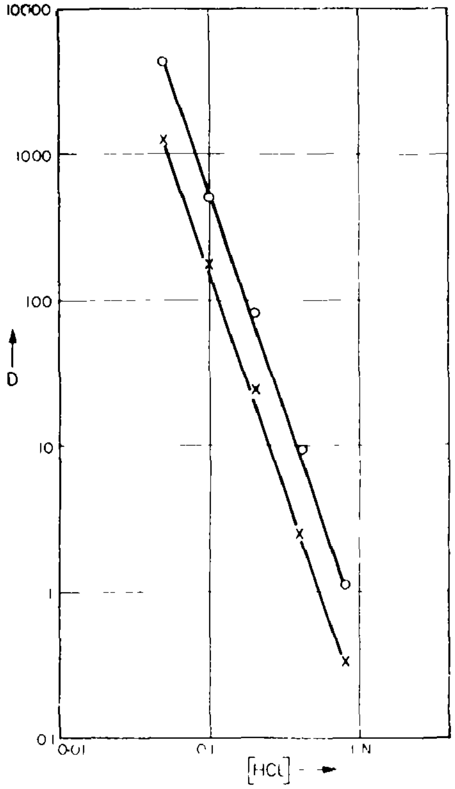


FIG 4 —Extraction of $\left\{\begin{matrix} Eu^{3+} \\ Am^{3+} \end{matrix}\right\}$ from HCl by 3×10^{-3} F HDOφP + 3×10^{-3} M DB[BP] in cyclohexane

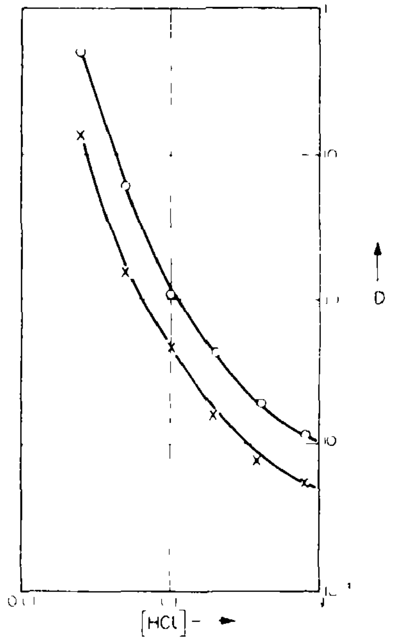


FIG 5 - Extraction of $\left\{\begin{matrix} Eu^{3+} \\ Am^{3+} \end{matrix}\right\}$ from HCl by 3×10^{-3} F HDOφP 0.3 M DB[BP] in cyclohexane

respectively No synergism was found for Tb and Lu The antisynergistic slope is − 2 for Eu and Am, −3 for Tb and Lu

(d) *Extraction of* Eu(III) *and* Am(III) *by* 0.003 *F* HDOφP + 0.003 *M* DB[BP] *in cyclohexane from varying concentrations of* HCl Fig 4 shows an inverse third power dependency of *D* on [HCl]

(e) *Extraction of* Eu(III) *and* Am(III) *by* 0.003 *F* HDOφP + 0.3 *M* DB[BP] *in cyclohexane from varying concentrations of* HCl Fig 5 shows the dependency of *D* on [HCl] to vary gradually from inverse third to inverse first power

(f) *Extraction of* Ca(II) *from* 0.01 *N* HCl *by* 0.01 *F* HDOφP + *varying concentrations of* DEH[EHP] *in benzene or cyclohexane* and *by* 0.01 *F* HDOφP + *varying concentrations of* TOPO *in cyclohexane* Results are shown in Fig 6 In benzene, a maximum increase in *D* by a factor of ~2 was found for 0.01 M DEH[EHP] In cyclohexane, maxima were found for 0.008 M TOPO and 0.02 M DEH[EHP], the factors being ~7 and ~5 respectively

(g) *Extraction of* Ca(II) *by* 0.01 *F* HnO[φP] + *varying concentrations of* DEH[EHP] *and of* Ba(II) *by* 0.01 *F* HDOφP + *varying concentrations of* DEH[EHP], *both in cyclohexane, from* 0.01 *N* HCl No synergism was found, as shown by Fig 7

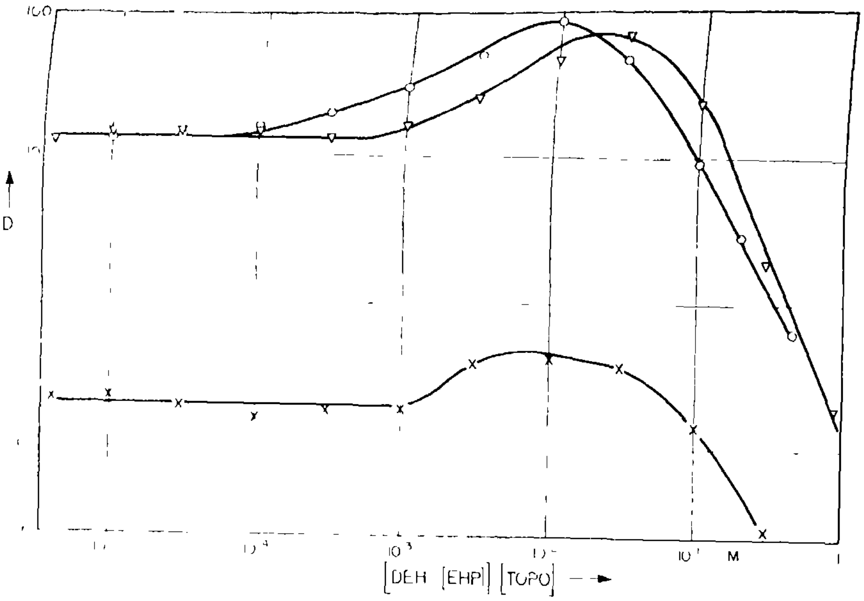


FIG. 6.—Extraction of Ca^{2+} from 0.01 N HCl by 10^{-2} F HDOφP +
○ TOPO in cyclohexane
▽ DEH[EHP] in cyclohexane
DEH[EHP] in benzene

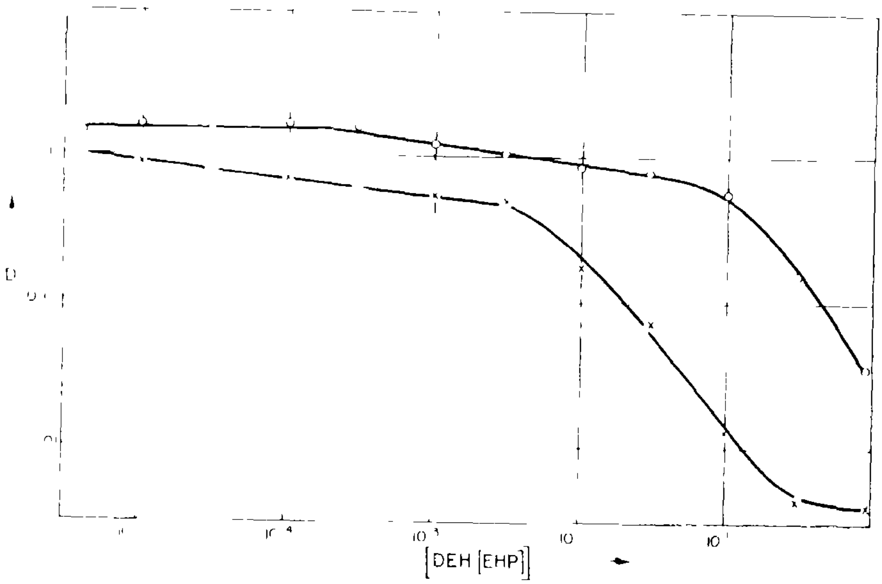


FIG. 7.—Extraction of { Ca^{2+} from 0.01 N HCl by 10^{-2} F HDO[φP] in cyclohexane
Ba^{2+} from 0.01 N HCl by 10^{-2} F HDOφP in cyclohexane

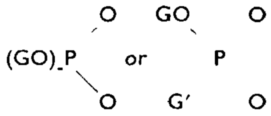
(h) *Extraction of* Ca(II) *from* 0.3 *N* HCl *by* 0.01 *F* HDOφP + *varying concentrations of* DEH[EHP] *or* TOPO *in cyclohexane*. Fig. 8 shows a maximum increase of *D* by a factor of ~2 for 0.004 M TOPO and 0.006 M DEH[EHP].

(i) *Extraction of* Th(IV) *by* 0.01 *F* HDEHP + *varying concentrations of* DEH[EHP] *or* TOPO *in cyclohexane from* 0.3 *N* HCl. Figure 9 shows a slight synergistic effect (increase of *D* by a factor of ~1.5) with maxima at 0.0001 M TOPO and 0.0002 M DEH[EHP]. The antisynergistic slope is approximately −2.

DISCUSSION

In the work on U(VI), the distribution ratios observed with the various chelating agents in the abence of synergist (at similar HCl and chelating agent concentrations) varied over a maximum factor of 40 (from $D_{\text{HEH[EHP]}}$ to $D_{\text{HEH[ClMP]}}$). For all other metal ions investigated, however, the spread of distribution ratios for various chelating agents includes several powers of 10. As an example, $D_{\text{HDO}\phi\text{P}}/D_{\text{HDEHP}}$ is 10^5 for Am(III)⁽⁹⁾ and 10^7 for Th(IV).⁽¹⁰⁾ Since, for the sake of accuracy, experiments should be limited to systems where $0.001 < D < 1000$, it was therefore mostly impossible in this study to compare different chelating agents for the same metal ion. Of course, different concentrations of chelating agent and/or of HCl could be used in order to obtain suitable values of *D*, but then the comparison would become meaningless. This work was therefore, with the exception of Ca, limited to the study of one chelating agent per metal ion.

Whenever *D* is so highly dependent on the nature of the chelating agent, the better extractants invariably appear to be these chelating agents which, from their structure, are expected to be the most acidic. This points to the extraction mechanism being simply an exchange of hydrogen ions and ions of the extracted metal without the additional formation of HXH^+ as for U(VI) (where X represents



and G, G′ any hydrocarbon radical).⁽¹,¹¹⁾ It may be assumed that, were it not for the formation of the ion HXH^+, which tends to favour extraction with the less acidic chelating agent, U(VI) would show a spread in values of *D* similar to that of other metal ions.

If a complex including HXH^+ is ruled out and taking into account the dimer state of the chelating agent,⁽¹²⁾ the third power dependency of *D* on the concentration of chelating agent $[(HX)_2]$ for all trivalent lanthanides and actinides⁽⁹⁾ can only be explained by the coordination of monoionized dimers HX_2^- (bidentate). It therefore appears likely that, unlike for U(VI), the mechanism proposed by BAES *et al.*⁽¹³⁾

⁽⁹⁾ D. F. PEPPARD, G. W. MASON, W. J. DRISCOLL and R. J. SIRONEN, *J. Inorg. Nucl. Chem.* **7**, 276 (1958).

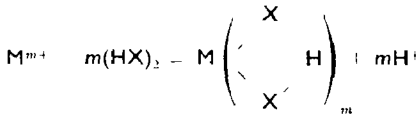
⁽¹⁰⁾ D. F. PEPPARD, G. W. MASON and S. MCCARTY, *J. Inorg. Nucl. Chem.* **13**, 138 (1960).

⁽¹¹⁾ J. KENNEDY and A. M. DEANE, *J. Inorg. Nucl. Chem.* **19**, 142 (1961).

⁽¹²⁾ D. F. PEPPARD, J. R. FERRARO and G. W. MASON, *J. Inorg. Nucl. Chem.* **7**, 231 (1958).

⁽¹³⁾ C. F. BAES JR., R. A. ZINGARO and C. F. COLEMAN, *J. Phys. Chem.* **62**, 129 (1958).

(mechanism B in the preceding paper) fully represents the extraction of trivalent lanthanides and actinides

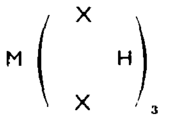


$$M^{m+} + m(HX)_2 \rightleftharpoons M\left(\begin{matrix} X \\ \quad H \\ X \end{matrix}\right)_m + mH^+$$

(in this case m = 3) This is the only model compatible with the generally assumed co-ordination number six for all lanthanides However, Fig 1 and 3 show a total difference in behaviour between lanthanides belonging to the first half of the group (La, Eu) and actinides on one hand, and lanthanides belonging to the second half (Tb, Tm, Lu) on the other This should be seen in correlation with the non-monotonic variation of D with Z, found in solvent extraction of lanthanides[(14)] and the half-filled shell hypothesis[(15)] It is therefore suggested that

(1) Lanthanides with $Z < 64$ (also actinides) have a maximum co-ordination number of eight while those with $Z > 64$ have only the co-ordination number six

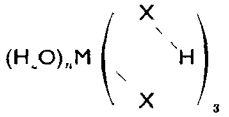
(2) *For the latter, the extracted species is*



$$M\left(\begin{matrix} X \\ \quad H \\ X \end{matrix}\right)_3$$

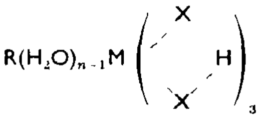
as represented above, *no synergism is possible here*

(3) Where the maximum co-ordination number is eight, the extracted species in the absence of synergist is



$$(H_2O)_nM\left(\begin{matrix} X \\ \quad H \\ X \end{matrix}\right)_3$$

where n = 1 or 2, and in the case of synergistic extraction



$$R(H_2O)_{n-1}M\left(\begin{matrix} X \\ \quad H \\ X \end{matrix}\right)_3$$

where R = synergist No complex containing 2 R is suggested, since in that case a stronger increase in D (theoretically, a slope of +2 on a log–log plot) with increasing synergist concentration should be expected

As in the case of U(VI), the antisynergism is due to the formation of a complex between R and $(HX)_2$

Using the methods developed in the preceding paper,[(1)] we obtain

(*a*) for lanthanides with $Z > 64$

$$M^{3+}_{aq} + 3(HX)_{2\,org} \rightleftharpoons M(HX_2)_{3\,org} + 3H^+_{aq}$$

$$(HX)_2 + R \quad (HX)_2R$$

[(14)] D F PEPPARD, W J DRISCOLL, R J SIRONEN and S McCARTY, *J Inorg Nucl Chem* **4**, 326 (1957)

[(15)] H BOMMER, *Z Anorg Chem* **241**, 273 (1939)

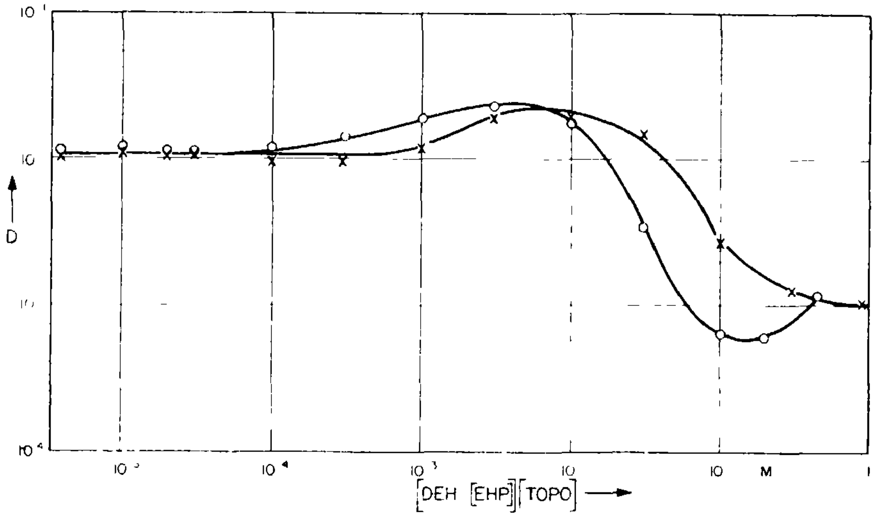


FIG 8—Extraction of Ca^{2+} from 0 3 N HCl with 10 F HDOφP
( ) TOPO
( ) DEH[EHP]] in cyclohexane

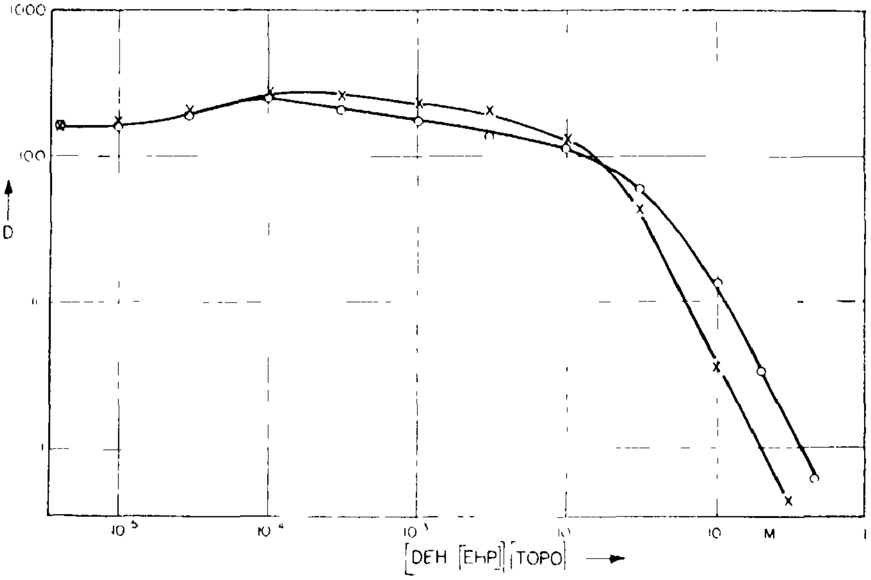


FIG 9—Extraction of Th^{4+} from 0 3 N HCl by 10 - F HDEHP (TOPO) (DEH[EHP]) in cyclohexane

with
$$K_M = \frac{[M(HX_2)_3]_{or}[H^+]^3_{aq}}{[M^{3+}]_{aq}[(HX)_2]^3_{or}} \quad (a\text{-}1)$$

or
$$K' = \frac{K_M}{[H^+]^3_{aq}} = \frac{D}{[(HX)_2]^3_{or}} \quad (a\text{-}1'), \qquad K = \frac{[(HX)_2R]}{[(HX)_2][R]} \quad (a\text{-}2),$$

and
$$D = \frac{K'}{K^3}\,\frac{[(HX)_2R]^3}{[R]^3} \quad (a\text{-}5)$$

At the limit of high synergist concentration, where [R] can be identified with $[R_{total}]$ and $[(HX)_2]R$ with $[(HX)_{2total}]$ = constant, the plot of D vs. $[R_{total}]$ on a log–log scale should show a −3 slope, as observed.

(b) for lanthanides with $Z \geq 64$ and trivalent actinides

$$M_{aq}^{3+} + 3(HX)_{2\,or} + R_{or} \rightleftharpoons M(HX_2)_3R_{or} + 3H^+_{aq} \quad (H_2O \text{ being disregarded})$$

with
$$K_M = \frac{[M(HX_2)_3R]_{or}[H^+]^3_{aq}}{[M^{3+}]_{aq}[(HX)_2]^3_{or}\,[R]_{or}} \quad (b\text{-}1)$$

or
$$K' = \frac{K_M}{[H^+]^3_{aq}} = \frac{D}{[(HX)_2]^3_{or}\,[R]_{or}} \quad (b\text{-}1'), \qquad (b\text{-}2) \equiv (a\text{-}2),$$

$$[(HX)_{2total}] = [(HX)_2]_{or} + [(HX)_2R] + 3[M(HX_2)_3R] \quad (b\text{-}3)$$

and
$$[R_{total}] = [R]_{or} + [(HX)_2R] + [M(HX_2)_3R] \quad (b\text{-}4)$$

From (b-1′) and (b-2),
$$D = \frac{K'}{K^3}\,\frac{[(HX_2R]^3}{[R]^2} \quad (b\text{-}5),$$

which explains the observed antisynergistic slope of −2. Neglecting the last term in (b-3) and (b-4), eliminating all terms relating to species of R between the equations and maximizing $D = f([(HX)_2]_{or})$ obtained in this way, the following expressions are derived:

$$[(HX)_2]_{or\,max} = \tfrac{2}{3}[(HX)_{2\,total}]$$

$$[R_{total}]_{max} = \tfrac{1}{3}[(HX)_{2\,total}] + \frac{1}{2K}$$

$$D_{max} = \frac{4K'}{27K}\,[(HX)_{2\,total}]^3$$

where the subscript (max) refers to the values at D = maximum.

The following values are now found for the system HDOφP–DB[BP]: $K \sim 600$, in good agreement with the result obtained before[(1)]; $K_{La}' \sim 1 \times 10^{11}$, $K_{Eu}' \sim 4 \times 10^{11}$, $K_{Am}' \sim 1 \times 10^{11}$, $K_{Cm}' \sim 6 \times 10^{10}$. For the system HDO$\varphi$P–TOPO, K is too high to be determined by this method, hence the values of K' could not be derived.

In order to establish whether any species is extracted in which HX_2^- is replaced by Cl^-, as would happen in extraction by the synergist alone, the dependency of D_{Eu} and

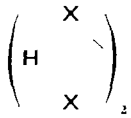
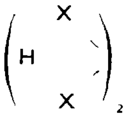
D_{Am} on $[\mathrm{HCl}]_{\mathrm{aq}}$ was determined for concentrations of chelating agent and synergist corresponding to the top and the bottom of the antisynergistic slope In the first case, the inverse third power dependency shows the absence of any participation by Cl^- in the extracted species At high concentrations of synergist, however, increased HCl concentration causes an increased participation of the "neutral extraction mechanism"

Extraction of alkaline earth metals by monoacidic phosphate or phosphonate esters has been shown(10) to be possible according to two mechanisms

(a), in which D is proportional to $[(\mathrm{HX})_2]^3$

(b), in which D is proportional to $[(\mathrm{HX})_2]^{5/2}$

Taking into account the maximum co-ordination number six and the inverse second power dependency of D on aqueous acidity, and ruling out any complex involving HXH^+ (see above), the only satisfying structures for the extracted species appear to be

(a)  M 2HX and (b)  M HX $\mathrm{H_2O}$

Extraction mechanism (b) is found to take place with bulky, acidic chelating agents like HDOφP in the extraction of Ca and Sr, while mechanism (a) prevails with smaller, less acidic chelating agents like HDEHP and HnO[φP], and in the extraction of Ba for all chelating agents If, by analogy with the lanthanides, synergism is expected to occur only where R can replace $\mathrm{H_2O}$ in the extracted species, then the extraction of species with (b) structures should show an increase in D on addition of a synergist, while synergism should be impossible for systems involving only (a) structures These predictions were completely borne out by experimental results

Applying again the method of calculation used for the extraction of U(VI)(1) and trivalent rare earths, the following equations are obtained for case (b)

$$\mathrm{M}^{2+}_{\mathrm{aq}} + \tfrac{5}{2}\,(\mathrm{HX})_{2\,\mathrm{or}} + \mathrm{R}_{\mathrm{or}} \quad \mathrm{M(HX_2)_2\,HX\,R_{or}} + 2\mathrm{H}^+_{\mathrm{aq}}$$

$$K_{\mathrm{M}} = \frac{[\mathrm{M(HX_2)_2\,HX\,R}]_{\mathrm{or}}[\mathrm{H}^+]^2_{\mathrm{aq}}}{[\mathrm{M}^{2+}]_{\mathrm{aq}}[(\mathrm{HX}_2]^{5/2}_{\mathrm{or}}\;[\mathrm{R}]_{\mathrm{or}}} \quad \text{or} \quad K' = \frac{K_{\mathrm{M}}}{[\mathrm{H}^+]^2_{\mathrm{aq}}} = \frac{D}{[(\mathrm{HX})_2]^{5/2}_{\mathrm{or}}\;[\mathrm{R}]_{\mathrm{or}}}$$

$$K = \frac{[(\mathrm{HX})_2\mathrm{R}]}{[(\mathrm{HX})_2][\mathrm{R}]} \text{ as above hence } D = \frac{K'}{K^{5/2}}\;\frac{[(\mathrm{HX})_2\mathrm{R})^{5/2}}{\mathrm{R}^{3/2}}$$

and therefore, at high synergist concentrations, an antisynergistic slope of −1 5 should be observed

Further,

$$[(\mathrm{HX})_{2\,\mathrm{total}}] = [(\mathrm{HX})_2]_{\mathrm{or}} + [(\mathrm{HX})_2\mathrm{R}] + \tfrac{5}{2}[\mathrm{M(HX_2)_2\,HX\,R}]$$

$$[\mathrm{R}_{\mathrm{total}}] = [\mathrm{R}] + [(\mathrm{HX})_2\mathrm{R}] + [\mathrm{M(HX_2)_2\,HX\,R}]$$

---

(10) D F Peppard G W Mason S McCarty and F D Johnson *J Inorg Nucl Chem* **24**, 321 (1962)

and by the "maximum method"

$$[(\mathrm{HX})_2]_{\max} = \tfrac{3}{5}[(\mathrm{HX})_{2\,\mathrm{total}}]$$

$$[\mathrm{R}_{\mathrm{total}}]_{\max} = \tfrac{2}{5}[(\mathrm{HX})_{2\,\mathrm{total}}] + \frac{2}{3K}$$

$$D_{\max} = \frac{6\sqrt{(3)}K'}{25\sqrt{(5)}K}[(\mathrm{HX})_{2\,\mathrm{total}}]^{5/2}$$

By examination of the results obtained in the extraction of Ca from 0.3 N HCl, it is found that

(1) the antisynergistic slope is in agreement with the predicted value

(2) $K_{\mathrm{HDO}\varphi\mathrm{P-DEH[EHP]}} \sim 330$, in fair agreement with the value of ~400 found in extraction of U(VI)(1)

(3) For the system HDOφP DEH[EHP], $K'_{\mathrm{Ca}} \sim 4 \times 10^6$

(4) As in the extraction of U(VI) and trivalent rare earths, *K* for the system *HDOφP–TOPO, and hence K′* cannot be calculated

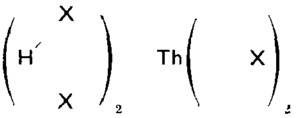
Several facts, however, remain unexplained

(1) Neither the antisynergistic slope, nor the value of $[\mathrm{R}_{\mathrm{total}}]_{\max}$ agree with the predicted values for the extraction of Ca by HDOφP from 0.01 N HCl (The latter aqueous acidity was used because it provided a suitable range of distribution ratios for both Ca and Ba)

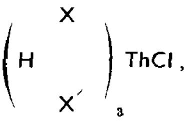
(2) The antisynergistic slope for extractions following mechanism (*a*) (Ca HDO[φP], Ba–HDOφP) falls short of the expected −3

(3) The synergistic effect appears to be much stronger at low aqueous acidity

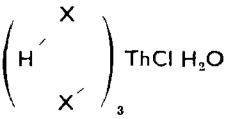
The extraction by HDEHP of Th(IV) from HCl solutions of the order of 0.3 N has been shown(10) to proceed either via the species



(with inverse fourth power dependency of *D* on $[\mathrm{H}^+]_{\mathrm{aq}}$) or via the species



or possibly



(showing an inverse third power dependency of *D* on $[\mathrm{H}^+]_{\mathrm{aq}}$) In view of the results for alkaline earths and trivalent rare earths, it seems likely that synergism will occur only in the latter case, where R can replace H_2O

Since the extracted complex $\mathrm{Th(HX_2)_3ClR}$ is, but for the chloride ion, similar to the species obtained by synergistic extraction of trivalent rare earths, similar results with respect to antisynergistic slope and values at *D* -- maximum should be obtained in both cases While this was found to be true for the slope (−2), the low $[R_{total}]_{max}$ obtained is in complete disagreement with calculations, since it is expected to exceed $\frac{1}{3}[(HX)_{2\,total}]$ It may be argued, however, that for a synergistic effect as small as shown by Th, the assumption that the extent of extraction not involving synergist is negligible with respect to the synergistic extraction is no longer true In that case the "maximum method" cannot be applied for Th

As a final argument for the fundamental difference between synergism in the extraction of U(VI) and of other metal ions, the synergistic performance of the phosphonates DEH[EHP] and DB[BP] should be compared to that of TOPO For U(VI), where synergistic extraction involves the formation of the ion HR^+ or $HXHR^+$, the D_{max} values obtained with the much more basic TOPO are at least ten times higher than with DB[BP] The fact that D_{max} for TOPO exceeds D_{max} for the phosphonate synergists only by a factor of 1 5 at most in the extraction of rare earths Ca and Th makes it likely that the synergist here performs some other function than complexing a hydrogen ion

Acknowledgement -The author wishes to thank, the International Atomic Energy Agency, Vienna and the Israel Atomic Energy Commission, for grants which made this work at Argonne National Laboratory possible, D F PEPPARD and G W MASON, Argonne National Laboratory for suggesting the problem, supplying the chelating agents, synergists and purified tracers, and offering further valuable help and encouragement in the course of this work, and T V HEALY, for helpful discussion

J. Inorg. Nucl. Chem. 1963. Vol. 25. pp. 1065 to 1069. Pergamon Press Ltd. Printed in Northern Ireland

NOTES

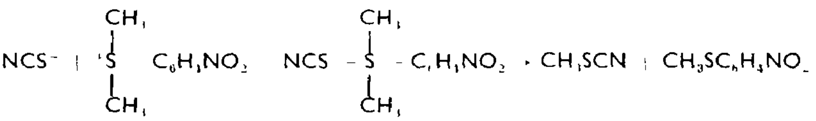
Reaction of sodium Π-cyclopentadienyldicarbonylferrate(O) with trimethylsulphonium iodide. Trimethylsulphonium salts as methylating agents

(*Received* 5 *March* 1963)

THE REACTION of trimethylchlorosilane with sodium π-cyclopentadienyldicarbonylferrate(O) π-$(C_5H_5)Fe(CO)_2Na$, has been reported(1) to yield π-cyclopentadienyltrimethylsilyldicarbonyliron(O) π-$(C_5H_5)Fe(CO)_2Si(CH_3)_3$, in which there is a direct bond between iron and silicon. It seemed reasonable to expect that, because of the ability of tetravalent sulphur to expand its valence level, similar compounds involving the trimethylsulphonium group could be made. Hence the reaction cited in the title was carried out in the hope of producing π-$C_5H_5Fe(CO_2)S(CH_3)_3$, with a direct bond between iron and the sulphonium sulphur atom. However it was found that the reaction produced instead methyl-π-cyclopentadienyldicarbonyliron, π-$C_5H_5Fe(CO)_2CH_3$ and dimethyl sulphide

$$\pi\text{-}C_5H_5Fe(CO)_2Na + (CH_3)_3SI \rightarrow \pi\text{-}C_5H_5Fe(CO)_2CH_3 + (CH_3)_2S + NaI$$

This reaction may involve the sought-for compound as an intermediate. A similar reaction between p-nitrophenyldimethylsulphonium ion and thiocyanate ion has been reported.(2)



$$NCS^- + {}^+S(CH_3)_2C_6H_4NO_2 \rightarrow NCS-S(CH_3)_2-C_6H_4NO_2 \rightarrow CH_3SCN + CH_3SC_6H_4NO_2$$

Several attempts to make triphenylsulphonium bromide react with the sodium salt have been made, but in all cases the unchanged sulphonium salt was recovered quantitatively.

Experimental

Preparation of $[(\pi$-$C_5H_5)Fe(CO)_2]_2$. This compound was prepared by the method of HALLAM, MILLS and PAUSON,(3) and was obtained upon recrystallization from methanol as red-purple crystals.

Preparation of $(\pi$-$C_5H_5)Fe(CO)_2Na$. One gram of the above compound was dissolved in 50 ml of methanol and treated with 40 g of 2% sodium amalgam. The mixture was stirred rapidly for 3 hr in an atmosphere of nitrogen and the solution was used directly for subsequent reaction.

Reaction between π-$(C_5H_5)Fe(CO)_2Na$ *and* $(CH_3)_3SI$. A solution of trimethylsulphonium iodide (1 g) in methanol (50 ml) was then added to the above solution of $(C_5H_5)Fe(CO)_2Na$ and the mixture stirred for about 12 hr. The solvent was removed in vacuum and the residue left was sublimed in vacuum at 70–100°C. A caramel-coloured waxy sublimate (m.p. 76–80°C) was obtained. The compound had a camphor-like odour and was soluble in most organic solvents giving yellow solution. The compound, either in the solid state or in solution, was found to be slowly decomposed by air. The infrared spectrum was identical with that of π-$(C_5H_5)Fe(CO)_2CH_3$.(4) Molecular weight determination in benzene and analysis for iron confirmed that the sublimate was π-$(C_5H_5)Fe(CO)_2CH_3$.

---

(1) T. S. PIPER, P. LEMAL and G. WILKINSON, *Naturwissenschaften* 43, 129 (1956).

(2) B. A. BOLTO and J. MILLER, *J. Org. Chem.* 20, 558 (1955).

(3) B. F. HALLAM, O. S. MILLS and P. L. PAUSON, *J. Inorg. Nucl. Chem.* 1, 313 (1955).

(4) T. S. PIPER and G. WILKINSON, *J. Inorg. Nucl. Chem.* 3, 104 (1956).

During vacuum sublimation dimethylsulphide was found to be collected in the trap which was ke cooled in dry ice acetone mixture

Acknowledgment The authors are grateful for the support of this work by the U S Borax Researc Corporation Subcontract No 3 under Air Force Prime Contract No AF 33(616)5931

The Department of Chemistry,
Purdue University,
Lafayette Indiana

A F Clifford
A K Mukherjee

The synthesis of 1-nitro-2-(n-oxy-n'-fluorodiazine) tetrafluoroethane*

(*Received* 26 *December* 1962)

A new compound containing the functional group —NONF[1] has been synthesized It is of intere inasmuch as it contains the two electronically similar groups NO_2 and —NONF The compound $O_2NC_2F_4NONF$, which is synthesized by the reaction of $O_2NC_2F_4NO$ and N_2F_4 in the gas phas

The N_2F_4 used was of about 99% purity The $O_2NC_2F_4NO$ was prepared by the addition of N to C_2F_4[2] at ambient temperature and purified by gas chromatography An initial purification w made on a 10 ft column of di-n-decylphthalate on C-22 firebrick (15 100) Final purification was b means of a similar 25 ft column Column conditions were ambient temperature and a helium flow about 50 cm³/min

The syntheses were carried out by sealing equal molar volumes of $O_2NC_2F_4NO$ and N_2F_4 in a evacuated Pyrex bomb Typical yield data are listed in Table 1

Table 1 $O_2NC_2F_4NONF$ yield data

Total pressure of reactants (cm Hg)	Reaction temp (°C)	Time (hr)	Yield (%) $O_2NC_2F_4NONF$	Completion of reaction (%)
26	~25	40	52	87
26	~25	74	67	98
30	71-73	5½	20	88
33	100	¼	27	~95
67	100	½	32	92

The $O_2NO_2F_4NONF$ was purified by gas chromatography using a 10 ft di-n-decylphthalat column as described above

The compound $O_2NC_2F_4NONF$ was identified by its mass spectrum, infrared spectrum an molecular weight A molecular weight of 208 1 was obtained by the method of limiting densities, a compared to 209 0 calculated The mass spectrum showed a very small peak at m/e = 209 Table lists some of the more important ions and their relative abundance Figure 1 is the infrared spectru at 1 4 cm pressure

* Work performed under the auspices of the U S Atomic Energy Commission

(1) J W Frazer, B E Holder and E F Worden, *J Inorg Nucl Chem* **24**, 45 (1962)

(2) J M Birchall, A J Bloom, R N Haszeldine and C J Willis, *Proc Chem Soc* 367, 36 (1959)

TABLE 2.—MASS SPECTRUM DATA FOR $O_2NC_2F_4NONF$

m/e	Ion	Relative abundance
30	NO	100
31	CF	16.1
33	NF	1.6
44	N_2O	0.9
46	NO_2	20.8
47	N_2F	17.6
50	CF_2	9.9
96	CF_2NO_2	0.3
100	C_2F_4	14.0
113	CF_2NONF	0.1
209	$O_2NC_2F_4NONF$	Trace

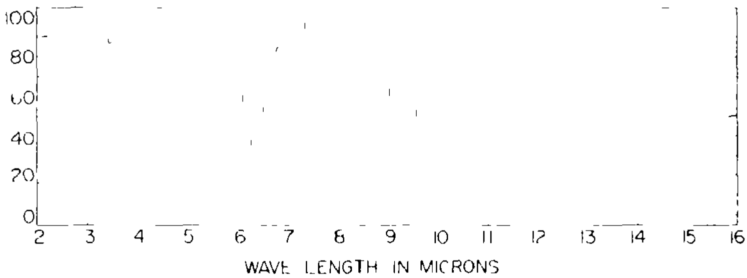


FIG. 1. Infrared spectrum of $O_2NC_2F_4NONF$ at 1.4 cm pressure

The vapour pressure of $O_2NC_2F_4NONF$ was measured between 16 C and 76.5 C and fit to the ANTOINE[3] equation

$$\text{Log}\ P_{\text{mm}}\quad 6.84935\quad [1115.5/(T\quad 67.84)]$$

The calculated boiling point is 75.8 C and the melting point is 50.8 0.3 C. This boiling point may be 1 2 C low due to slight decomposition at ambient temperatures in the isoteniscope.

This compound was found to be relatively stable when handled in small amounts in a glass vacuum apparatus lubricated with Kel-F grease. However, on one occasion when about 1.5 g of the reaction products melted and the liquid phase at about 0 C contacted the Kel-F grease, a violent explosion occurred.

Lawrence Radiation Laboratory
University of California
Livermore, California

J. W. FRAZER
V. I. DUVAL

---

[3] D. G. MILLER, Report UCRL-6862 (1962).

The thermal decomposition of Ni (pyridine)$_4$ Cl$_2$ and the preparation of Ni (pyridine) Cl$_2$

(*Received* 16 *March* 1963; *in revised form* 1 *April* 1963)

TETRAKISPYRIDINE nickel(II) halides and bispyridine nickel(II) halides are well known and, in common with anhydrous nickel chloride, have structures in which the nickel ion is octahedrally co-ordinated. It has now been found that $Ni(py)_2Cl_2$ (py pyridine) decomposes to $NipyCl_2$ at 190 and that the latter complex also contains nickel ions in octahedral co-ordination.

The thermal decomposition curve of $Ni(py)_4Cl_2$ (determined on a Stanton Thermogravimetric Balance chart speed 6 in /hr) shows four definite stages corresponding to $Ni(py)_4Cl_2$ (Mol wt calc 446), $Ni(py)_2Cl_2$ (Eq wt Found 285 Calc 288) $NipyCl_2$ (Eq wt Found 208, Calc 209), and $NiCl_2$ (Eq wt Found 131 Calc 130) The three decomposition temperatures as shown in Fig 1 are 110°, 190° and 310° and the specimens achieved constant weight as $NiCl_2$ at 360° Specimens of $Ni(py)_2Cl_2$ and $NipyCl_2$ were also prepared by heating samples of $Ni(py)_4Cl_2$ for 1 hr to 190° and 310° respectively (Found Ni 20.3 C 42.0 H 3.4 N, 9.5 Cl, 25.0 $Nipy_2Cl_2$ requires Ni 20.5, C, 41.8 H 3.5 N 9.7 Cl 24.7%, Found Ni 27.7 C 31.4 H 2.2 N, 6.4 Cl 33.6 $NipyCl_2$ requires Ni 28.2 C 28.8 H 2.4 N 6.7 Cl 34.0%.) Slight charring occurred during the preparation of $NipyCl_2$ and this is reflected in the carbon analysis X-ray powder photography showed that $NipyCl_2$ is a separate and distinct entity

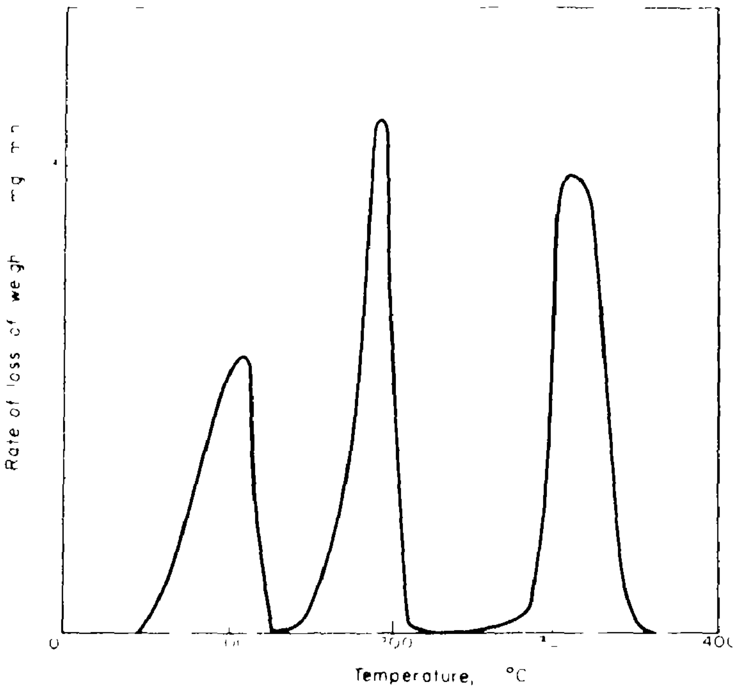


Fig. 1 The thermal decomposition of $Ni(py)_4Cl_2$

The reflectance spectra of all the samples were taken on a Hilger Uvispek Spectrophotometer and the results are compared with literature values for $Ni(py)_4Cl_2$ $Ni(py)_2Cl_2$ and $NiCl_2$ in Table 1 The spectra observed for these latter compounds are in good agreement with published values and the spectrum found for $NipyCl_2$ fits into the series suggesting that the environment around each nickel atom is an octahedron of five chlorine atoms and one nitrogen atom The infrared spectrum of $NipyCl_2$ in the sodium chloride region confirms the presence of pyridine as a ligand and the absence in the caesium bromide region of metal-chloride bands at about 310 cm^{-1} is in favour of an octahedral environment about the nickel atom (1) Assuming an octahedral environment about the nickel there seem to be two possible arrangements of atoms which would give the required stoichiometry One has two chlorine atoms each acting as a bridge between two nickel atoms and three chlorine atoms each acting as a bridge between three nickel atoms and the other has one chlorine atom unbridged and four chlorine atoms each acting as a bridge between four nickel atoms

Thermal decomposition of other pyridine nickel halides does not proceed by way of monopyridine nickel complexes

(1) D H Brown R H Nuttall, and D W A Sharp, unpublished work

TABLE 1 THE REFLECTANCE SPECTRA OF PYRIDINE NICKEL CHLORIDES
(Figures in $cm^{-1} \times 10^{-3}$)

Compound	Environment	$^3\Gamma$	$^3\Gamma_4$	$^1\Gamma_3$	$^1\Gamma_5$	$^3\Gamma_4$
$Nipy_4Cl_2$[a]	4N 2Cl	10.9	16.0	13.1		25.8
$Nipy_2Cl_2$[a]	2N 4Cl		14.0	12.8	23.0	24.2
$NipyCl_2$[a]	1N 5Cl		13.3	12.1	20.8	23.8
$NiCl_2$[a]	6Cl		13.0	11.6	19.6	22.3
	Literature values					
$Nipy_4Cl_2$[b]	4N 2Cl	10.9	15.9			25.7
$Nipy_2Cl_2$[c]	2N 4Cl		14.1		23.0	24.1
$NiCl_2$[d]	6Cl		12.9	11.6	19.4	22.1

(a) Present work

(b) O BOSTRUP and C K JORGENSEN *Acta Chem Scand* **11**, 1223 (1957)

(c) E KONIG and H L SCHLAFER *Z phys Chem* **26**, 371 (1960)

(d) R W ASMUSSEN and O BOSTRUP *Acta Chem Scand* **11**, 745 (1957)

We thank the Royal Society for a grant for the purchase of a far infrared spectrophotometer and the Department of Scientific and Industrial Research for the award of a Senior Fellowship (to R H N)

Chemistry Department
The Royal College of Science and Technology
Glasgow C 1

D H BROWN
R H NUTTALL
D W A SHARP

Exchange properties of ammonium salt of 12-heteropolyacids—VI. Sorption of cerium, ruthenium, zirconium and niobium on ammonium phosphotungstate and isolation of ^{137}Cs from an aged mixture of fission products

(*Received* 17 *December* 1962, *in revised form* 8 *April* 1963)

FEW references can be found to the sorption of poly-valent fission products on ammonium salts of heteropolyacids, although SMIT *et al* (1) have described the separation of fission products on ammonium phosphomolybdate Our previous paper(2) describe the sorption of ^{90}Sr ^{90}Y on NH_4PW and their separation from caesium and in this study the sorption of other long-lived fission products (Ce Ru Zr) on NH_4PW and the isolation of ^{137}Cs from fission products solution were examined

Experimental

Ammonium phosphotungstate with the composition $(NH_4)_{2.80}H_{0.20}[P(W_{12}O_{40})]\ 12.8\ H_2O$ was prepared and analysed as described previously(3), experimental procedures have also been described (2-4) ^{144}Ce ^{106}Ru ^{95}Zr ^{95}Nb tracers were of Soviet origin, and ^{90}Y was separated from ^{90}Sr by extraction with TTA Labelled ruthenium as nitrate and nitrosylruthenium tri-nitrate was employed (6,7)

[1] J VAN R SMIT W ROBB and J J JACOBS, *Nucleonics* **17**, 116 (1959)

[2] J KRTIL *J Inorg Nucl Chem* **22**, 247 (1961)

[3] J KRTIL and V KOUŘIM, *J Inorg Nucl Chem* **12**, 367 (1960)

[4] J KRTIL, *J Inorg Nucl Chem* **19**, 298 (1961)

[5] R A BOLOMEY and L WISH, *J Amer Chem Soc* **72**, 4483 (1950)

[6] J S ANDERSON and J D M McCONNELL, *J Inorg Nucl Chem* **1** 371 (1955)

[7] J M FLETCHER *et al* *J Inorg Nucl Chem* **1**, 378 (1955)

Sodium and ammonium ions were added as nitrates. All reagents were of analytical grade, and experiments were carried out at room temperature, the results being expressed in terms of distribution coefficients.

Results and Discussion

^{144}Ce

When the hydrogen ion concentration was varied both yttrium and cerium showed a linear relationship between log K_d and log [HNO_3] over the range 0.2 to 1 M nitric acid, the gradient being 3, indicating that the ions are sorbed by ion exchange. Cerium and the other rare earths are weakly held compared with the heavy alkali metals, and the sorption of rare earths is more strongly influenced by the presence of H^+ and Na^+ ions (Table 1). NH_4^+ ions have less effect.

TABLE 1 — EFFECT OF SODIUM AND AMMONIUM SALTS ON THE SORPTION OF ^{144}Ce BY NH_4PW AT pH 2.1

Salt	Concentration (M)	K_d*
		41
	0.15	176
NH_4NO_3	0.24	288
	0.75	1420
	1.50	2240
$NaNO_3$	0.30	1.2
	0.70	0.1

K_d = (c.p.m. per g of NH_4PW)/(c.p.m. per ml of solution)

^{106}Ru

Both ruthenium (IV) nitrate and nitrosylruthenium (III) trinitrate show a linear relationship between log K_d and log [H^+] from 0.4 to 6 M acid, the gradient for both forms being ~2. The effect of sodium and ammonium ions at constant acidity is shown in Table 2. In this case NH_4^+ ions exert a greater influence on the desorption of ruthenium than sodium salts.

TABLE 2 — EFFECT OF SODIUM AND AMMONIUM SALTS ON THE SORPTION OF RUTHENIUM (IV) NITRATE AND OF NITROSYLRUTHENIUM (III) NITRATE
[HNO_3] 0.4 M for $RuNO^{3+}$, 0.5 M for Ru^{4+}

Salt	Concentration (M)	K_d	
		$RuNO(NO_3)_3$	$Ru(NO_3)_4$
		9.6	
			63.6
	0.10	6.0	68.6
$NaNO_3$	0.30	2.8	19.2
	0.70	1.2	3.0
	1.20	0.02	2.6
NH_4NO_3	0.10	1.58	10.4
	0.28	0.18	1.26

^{95}Zr-^{95}Nb

The sorption of an equilibrium mixture of ^{95}Zr-^{95}Nb increases with increasing acidity, log K_d is a linear function of log [H^+] but the gradient is non-integral.

In acid solutions sorption of uncharged hydrolysed and complexed species may take place.(8) This explanation is supported by the effect of foreign salts (Table 3). Foreign ions (Na^+, NH_4^+) are seen to increase the sorption as in the molecular sorption of Zr/Nb, where the effect of foreign ions increases in the order $Na^+ < NH_4^+$.(8)

TABLE 3. EFFECT OF SODIUM AND AMMONIUM SALTS ON THE SORPTION OF ^{95}Zr–^{95}Nb
[HNO_3] = 0.25 M

Salt	Concentration (M)	K_d
	0.08	2.66
$NaNO_3$	0.39	4.0
	0.97	5.0
	0.10	380
NH_4NO_3	0.30	1280
	0.98	1190

Isolation of ^{137}Cs from synthetic aged mixed fission products

The principal activities in aged (2 yr) fission products are due to alkali metals, alkaline earth metals and rare earth elements.(10) ^{137}Cs was separated from a representative synthetic mixture by sorption in NH_4PW, washing the column with 12 M HCl (or HNO_3), 0.3 M NH_4NO_3 and elution of Cs with 10 M NH_4NO_3. β- and γ-spectrometry, using a 200-channel analyser (Intertechnika) showed the maximum impurity content to be 0.1% ^{106}Ru, 0.2% ^{144}Ce, ^{154}Eu, ^{90}Y, and 0.1% ^{90}Sr. Decontamination factors were found to be 5.7 × 10^3 for Ru, 1.5 × 10^4 for Ce, Eu and Y and 1 × 10^1 for Sr.

J. KRTIL
J. ZEMANOVÁ

Institute of Nuclear Research
Řež u Prahy
Czechoslovakia

(8) I. E. STARIK *et al.*, *Radiochimija* **1**, 370 (1959).
(9) I. E. STARIK, V. N. SHEBETKOVSKIJ and I. A. SKULSKIJ, *Radiochimija* **3**, 435 (1961).
(10) J. MALÝ *et al.*, *Čs. čas. fys.* **6**, 616 (1956).

ERRATA

A. D. Kirshenbaum, J. A. Cahill, P. J. McGonigal and A. V. Grosse *The density of liquid NaCl and KCl and an estimate of their critical constants together with those of the other alkali halides* *J. Inorg. Nucl. Chem.* **24**, 1287–1296 (1962)

Page 1293 line 2 below Table 7,

for "*upper limit*" read "*critical temperature*"

M. Zangen Some aspects of synergism in solvent extraction—I *Uranium (VI)*, *J. Inorg. Nucl. Chem.* **25**, 581–594 (1963)

Page 581, line 2

for "(the cheating agent)" read "(the chelating agent)"

Page 581 line 21

for "$\left(H\ \begin{matrix}X\\X\end{matrix}\right)_3 UO_2^{\ R}$" read "$\left(H\ \begin{matrix}X\\X\end{matrix}\right)_2 UO_2^{\ R}$"

Page 594, line 1

for "$(H^+)_{aq}^{2}$ hence to $(HCl)^2$" read "$(H^+)_{aq}^{-2}$ hence to $(HCl)^{-2}$"

rg. Nucl. Chem., 1963, Vol. 25, pp. 1073 to 1077. Pergamon Press Ltd. Printed in Northern Ireland

ISOMERIC YIELD RATIOS OF ^{44}Sc PRODUCED BY THE ^{14}N BOMBARDMENT OF ^{32}S AND ^{31}P

M. E. WETZEN
University of Tennessee
and
K. S. TOTH
Oak Ridge National Laboratory*

(*Received* 21 *January* 1963)

Abstract—Thick targets of red phosphorus and zinc sulphide were bombarded with 27.5 MeV ^{14}N ions accelerated in the Oak Ridge 63 in. Cyclotron. Cross sections, as a function of the bombarding energy, were measured for the production of ^{43}Sc, ^{44m}Sc, and ^{44g}Sc from ^{31}P and ^{32}S. The irradiated materials were γ-counted, and the radioactive products were identified by their characteristic γ-rays and half-lives. From the cross sections, the isomeric yield ratios of ^{44m}Sc/^{44g}Sc were found. For ^{31}P the isomer ratio varied from 0.68 at 23.5 MeV to 1.68 at 27.0 MeV, while for ^{32}S it varied from 0.12 at 20.5 MeV to 1.15 at 27.0 MeV. This increase in the ratio for both reactions is consistent with a compound nucleus formation mechanism for ^{44}Sc at all energies considered. Accordingly, the higher ratio in the phosphorus reaction than in the sulphur reaction may be attributed to the smaller amount of angular momentum taken off by the single proton emitted from the ^{31}P reaction than by the two protons emitted in the ^{32}S case.

ZINC sulphide and phosphorus were bombarded with 27.5 MeV triply charged ^{14}N ions, accelerated in the Oak Ridge National Laboratory 63 in. Cyclotron, to produce ^{44}Sc and ^{43}Sc. The primary purpose of the investigation was to obtain information concerning the reaction mechanism involved in the production of ^{44}Sc by studying the yield ratios of the two ^{44}Sc isomers as a function of bombarding energy. Other workers(1–4) have investigated the isomeric yield ratios of ^{44}Sc produced in neutron, proton, and alpha induced reactions. This isotope is a particularly convenient choice because of the wide separation in γ-ray energies and the large difference between the half-lives of the two isomeric states. The metastable state, ^{44m}Sc (6 or 7 +), has a γ-ray of 0.270 MeV and a half-life of 2.44 days,(5) the ground state, ^{44g}Sc (2 or 3 +), has a γ-ray of 1.159 MeV and a half-life of 3.9 hr.(5) It was also anticipated that the difference in the number of particles emitted in the two reactions, ^{31}P(^{14}N, p)^{44}Sc and ^{32}S(^{14}N, $2p$)^{44}Sc, would have some effect on the isomeric yield ratios.

EXPERIMENTAL METHOD

Targets were made by pressing zinc sulphide and red phosphorus at a pressure of 10 000 lb/in^2 into brass molds ¾ in. in diameter. These targets, thicker than the range of nitrogen ions, presented a hard uniform surface which did not change under bombardment. By comparing the relative yields of ^{18}F and ^{24}Na produced by the bombardment of a carbon target with the data of REYNOLDS and

---

* Operated for the U.S.A.E.C. by Union Carbide Corporation.

(1) J. W. MEADOWS, *Phys. Rev.* **102**, 190 (1956).

(2) R. J. PRESTWOOD and B. P. BAYHURST, *Phys. Rev.* **121**, 1438 (1961).

(3) T. MATSUO and T. T. SUGIHARA, *Canad. J. Chem.* **39**, 697 (1961).

(4) S. M. BAILEY, *Phys. Rev.* **123**, 579 (1961).

(5) *Nuclear Data Sheets*, National Academy of Sciences, National Research Council, Washington, D.C. (1960).

ZUCKER[6], the energy of the incident beam was determined to be 27.5 ± 0.5 MeV. This energy was varied by placing nickel foils in steps of approximately 0.6 mg/cm^2 between the beam and the target. From the range–energy relations of nitrogen on nickel[7] the energy of the beam hitting each target was calculated. The targets were bombarded in a Faraday cup assembly. Since the absorbers were placed directly in the Faraday cup, it was not necessary to consider the effective charge of the nitrogen ions after they passed through these foils. The beam current passing through a ½ in. collimator was approximately 0.20 μa for zinc sulphide and 0.065 μa for phosphorus. The volatile nature of phosphorus necessitated the smaller current.

After each bombardment, the target was removed from the mold, placed in a stainless steel cup, and counted with a 1½ × 1½ in. NaI(Tl) crystal γ-ray spectrometer connected to a 256-channel pulse height analyser. The efficiency of the NaI crystal was calibrated for the particular counting geometry by the use of several γ-ray standards. A relative photopeak efficiency curve was constructed from the known decay characteristics of ^{22}Na, ^{46}Sc, ^{58}Co, ^{59}Fe, ^{60}Co, ^{65}Zn, ^{88}Y, ^{115m}Cd and ^{125}Sb. This covered the γ-ray energy region from 0.18 to 1.8 MeV. The ^{22}Na source was then beta-counted in a shielded Geiger counter with a known counting efficiency to determine the absolute disintegration rate of the sample. The relative photopeak efficiency curve could then be converted into an absolute curve. The error in this latter curve was estimated to be ± 15 per cent. Proper corrections were made for the γ-ray branching ratios,[5] decay during bombardment, and beam intensity to obtain the absolute yields per incident particle. The identifying half-lives, γ-radiations, and the branching ratios used in calculating the reaction yields are shown in Table 1.

TABLE 1. IDENTIFYING γ-RAYS AND THEIR BRANCHING RATIOS

Isotope	Half-life	Gamma-ray energy (MeV)	Branching ratios (%)
^{44m}Sc	2.44 days	0.270 1.159	100.0 100.0
^{44g}Sc	3.9 hours	1.159	100.0
^{43}Sc	3.9 hours	0.374	21.6

RESULTS AND DISCUSSION

The yields per incident particle of ^{44m}Sc, ^{44g}Sc and ^{43}Sc from ^{31}P and ^{32}S were determined and plotted as a function of bombarding energy (Figs. 1 and 2). The scatter of the experimental points at a given energy indicates the relative error inherent in the thick target yields. This error arises from uncertainties in beam intensity, counting statistics, and in the energy of the incident ^{14}N beam. Smooth curves were then drawn through each set of experimental points and cross sections as a function of bombarding energy were determined by differentiating these smooth curves. For this determination, the stopping powers of ZnS and phosphorus for ^{14}N ions were calculated by the method described previously.[8,9] Excitation functions obtained in this manner are shown in Figs. 3 and 4. The error in the absolute cross sections is estimated to be about ±30%, this takes into account uncertainties in crystal calibration, γ-ray branching ratios, slope of the yield curves, and the calculated stopping powers.

FISHER *et al.*[10] investigated the production of ^{44}Sc from the ^{14}N bombardment of

---

[6] H. L. REYNOLDS and A. ZUCKER, *Phys. Rev.* **95**, 1615 (1954).
[7] H. L. REYNOLDS, D. SCOTT and A. ZUCKER, *Phys. Rev.* **95**, 671 (1954).
[8] W. H. WEBB, H. L. REYNOLDS and A. ZUCKER, *Phys. Rev.* **102**, 749 (1956).
[9] M. L. HALBERT, T. H. HANDLEY and A. ZUCKER, *Phys. Rev.* **104**, 115 (1956).
[10] D. E. FISHER, A. ZUCKER and E. GROPP, *Phys. Rev.* **113**, 543 (1959).

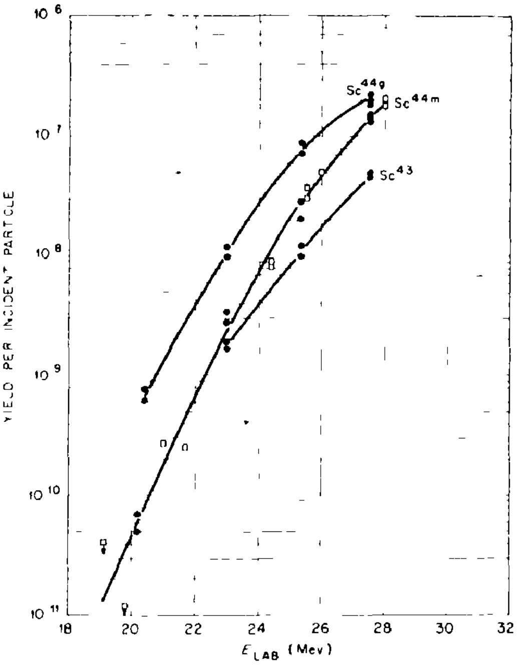


FIG. 1 —Yields per incident particle determined for ^{43}Sc, ^{44m}Sc and ^{44g}Sc resulting from the ^{14}N bombardment of ^{32}S. For ^{44m}Sc, squares represent the data of FISHER *et al.*(10)

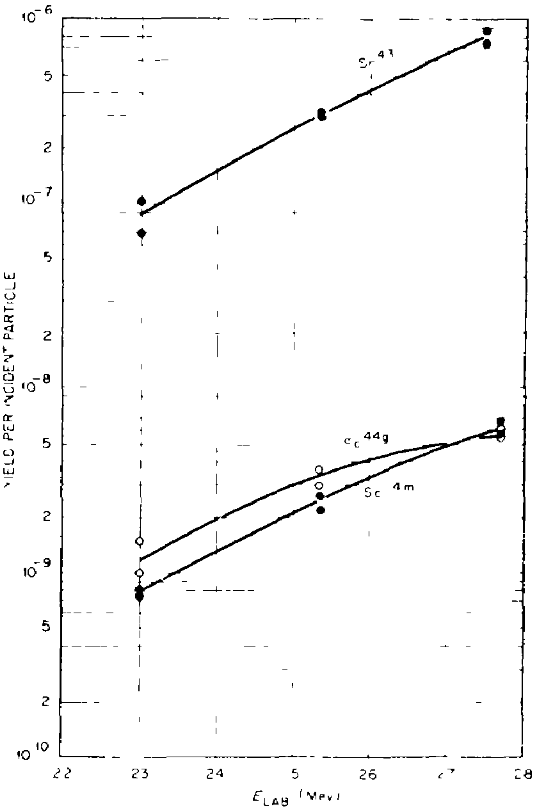


FIG. 2 — Yields per incident particle determined for ^{43}Sc, ^{44m}Sc and ^{44g}Sc resulting from the ^{14}N bombardment of ^{31}P.

^{32}S. Their ^{44m}Sc yield points shown in Fig. 1 (squares) are seen to agree very well with those obtained in this experiment. A smooth curve fitting all the available yield points was differentiated to determine the ^{44m}Sc excitation functions shown in Fig. 3. It is not possible to compare their data for ^{44g}Sc since they did not separate ^{43}Sc from ^{44g}Sc but instead obtained an excitation function for the total 3.9 hr scandium activity. However, at 28.0 MeV they determined from a γ-ray spectrum that ^{43}Sc was approximately 16 per cent of the total 3.9 hr activity. We found that ^{43}Sc accounted for ~18 per cent of the total 3.9 hr activity at 27.5 MeV, and ~13 per cent at lower bombarding energies.

NEWMAN and TOTH(11) bombarded ^{31}P with ^{14}N ions at 25.35 and 27.5 MeV. From the yields at these two energies they obtained a 56.4 mbarns cross section for the production of ^{43}Sc at 26.5 MeV. At the same energy we found the cross section to be 60.1 mbarns. The agreement between the two values is well within the limits of experimental error.

Figure 5 shows the isomer yield ratios (^{44m}Sc/^{44g}Sc) plotted vs E_{cm} for the phosphorus and sulphur reactions along with those obtained from the reaction ^{35}Cl(^{14}N, αp)^{44}Sc investigated earlier(11) at this Laboratory. Certain points concerning the

---

(11) F. NEWMAN and K. S. TOTH, *Phys. Rev.* **129**, 802 (1963).

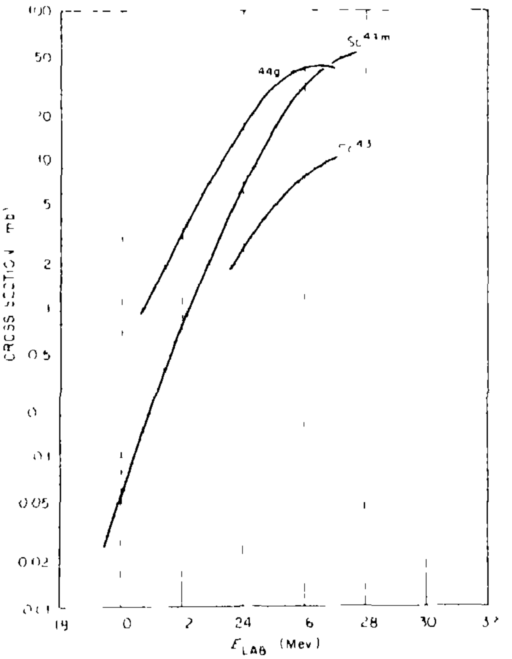


FIG. 3—Excitation functions for the production of ^{43}Sc, ^{44m}Sc and ^{44g}Sc from the ^{14}N bombardment of ^{32}S

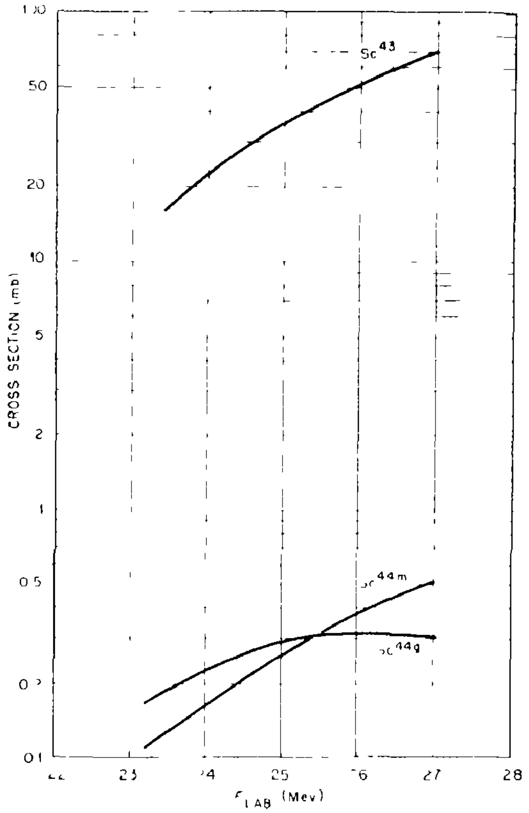


FIG. 4—Excitation functions for the production of ^{43}Sc, ^{44m}Sc and ^{44g}Sc from the ^{14}N bombardment of ^{31}P

three ^{14}N-induced reactions can be noted In the ^{31}P and ^{32}S reactions the isomer ratio increases steadily with energy, while the ratio for the ^{35}Cl reaction first increases with energy and then levels off at $E_{cm} \sim 18.6$ MeV Studies[3,4] of the reaction ^{41}K(α, n)^{44}Sc have shown the same isomer ratio first increasing with energy then turning over at $E_{cm} \sim 24$ MeV and finally decreasing at still higher energies The following explanation was offered for these results The initial increase of the ratio indicates a compound nucleus mechanism Because of the higher density of states at high energies of the residual nucleus, the compound system emits low-energy light particles with consequently little angular momentum carried off The residual nucleus is thus left with more angular momentum as the bombarding is increased and the isomer ratio would thus be expected to increase The subsequent decrease in the ratio indicates the onset of a direct reaction mechanism at higher energies In a direct process the residual nucleus is left in a lower state of excitation and with less angular momentum, the low-spin isomer would thus be favoured

It would then seem from the above discussion that the behaviour of the ^{32}S and ^{31}P reactions indicates a compound nucleus mechanism for the production of ^{44}Sc at the studied energies The gentler increase and subsequent leveling-off of the isomer ratio for the ^{35}Cl reaction might be explained in two ways First, the loss from the compound system (^{49}Cr) of a large amount of angular momentum, carried

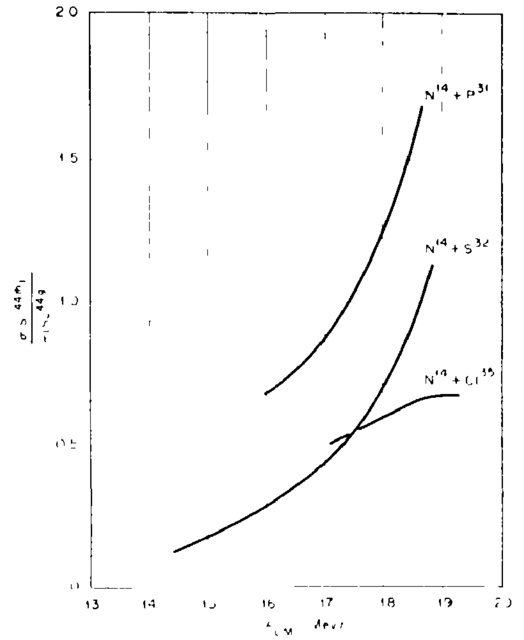


Fig. 5. Isomeric yield ratios of ^{44}Sc resulting from the ^{14}N bombardment of ^{31}P, ^{32}S and ^{35}Cl.

off by the alpha particle, should result in a higher yield of ^{44g}Sc from the chlorine reaction than for the ^{32}S and ^{31}P reactions. Second, perhaps some reaction mechanism other than compound nucleus formation is beginning to set in at $E_{cm} \sim 18.6$ MeV. Such a mechanism could account for the differences found between calculations based on the statistical model and experimental results obtained in (^{14}N, γ) reactions.$^{(10,11)}$

One can observe from Fig. 5 that the isomer ratio is higher for the phosphorus reaction than for the sulphur reaction at all energies investigated. This difference can also be observed in the excitation functions shown in Figs. 3 and 4. Here we note that the ^{44m}Sc and ^{44g}Sc curves cross at a higher energy (26.65 MeV) in the sulphur reaction than in the phosphorus reaction (25.30 MeV). Since both of these reactions bring essentially the same average angular momentum into the system (seven or eight units) the number of particles emitted from the compound nucleus in the two reactions may account for this difference in isomer ratios. The proton emitted in the phosphorus reaction would carry off less angular momentum than the two protons emitted in the sulphur reaction. One should then predict a higher yield of the high-spin isomer in the system left with more angular momentum—in this case the system produced in the ^{31}P reaction.

Acknowledgements—The authors wish to thank F. Newman who assisted in many phases of this experiment. They also wish to thank M. L. Halbert and A. Zucker for their helpful comments.

J. Inorg. Nucl. Chem., 1963, Vol. 25, pp. 1079 to 1083. Pergamon Press Ltd. Printed in Northern Ireland

DECAY OF ^{131}Ba–^{131}Cs

W. S. LYON
Analytical Chemistry Division, Oak Ridge National Laboratory,*
Oak Ridge, Tennessee

(*Received* 18 *February* 1963, *in revised form* 15 *March* 1963)

Abstract—The absolute intensities of eight γ-rays emitted following electron capture in ^{131}Ba have been determined: 0.130 MeV (0.28), 0.220 MeV (0.28), 0.380 MeV (0.16), 0.496 MeV (0.60), 0.600 MeV (0.032), 0.820 MeV (0.0034), 0.910 MeV (0.0009), and 1.04 MeV (0.017).

The method used was to prepare ^{131}Ba free from its ^{131}Cs daughter, allow the ^{131}Cs activity to grow in, separate the ^{131}Cs activity from the parent and measure its activity, measure the γ-activity of the ^{131}Ba by γ-ray spectrometry, and calculate the absolute amount of ^{131}Ba from parent daughter growth relationships. The half-life of ^{131}Cs has been determined to be 9.83 ± 0.28 days. The ratio of the pile neutron activation cross-sections for the production of ^{131}Ba and ^{133}Ba has been found to be $\sigma_{130}/\sigma_{132}$ = 1.36 ± 0.08.

GAMMA-RAYS following electron capture in ^{131}Ba have been studied by several investigators. BEGGS, *et al.*$^{(1)}$ identified at least nine gamma rays and made measurements of their relative intensities. AUGUST *et al.*$^{(2)}$ measured relative intensities of five of these γ-rays. Conversion coefficients for some of these γ-rays and the lifetime of a metastable state at 0.081 MeV have also been reported and are tabulated in nuclear data collections.$^{(3)}$ Very recently KELLEY and HOREN$^{(4)}$ report the conversion electron spectra of ^{131}Ba. No measurement has been made previously, however, on the absolute γ-ray intensities due primarily to the difficulty in measuring the disintegration rate of ^{131}Ba.

In the present work, the relative intensities of eight γ-rays associated with the decay of ^{131}Ba have been measured. The absolute intensities have been determined by measuring the active ^{131}Cs daughter of ^{131}Ba and back calculating to determine the amount of ^{131}Ba parent present. The half-lives of both ^{131}Cs and ^{131}Ba have been remeasured, and in addition, the ratio of the pile neutron activation cross-section for production of ^{131}Ba and ^{133}Ba ($\sigma_{130}/\sigma_{132}$) has been obtained.

EXPERIMENTAL

Barium-131 produced by neutron capture on natural barium in the Oak Ridge Research Reactor was used as a starting material in the barium–cesium separation work. To several millicuries of ^{131}Ba solution, a few milligrams of barium carrier was added and $BaCl_2$ precipitated by addition of HCl ether solution.$^{(5)}$ The precipitate was separated by centrifugation, redissolved in a few drops of H_2O and the separation repeated twice more. The time of the final $BaCl_2$ precipitation was noted. The $BaCl_2$ was dissolved in H_2O and made to a known volume. Cesium-131 was allowed to grow in for twelve days and then a barium–cesium separation was made using the following procedure:$^{(6)}$

---

* Operated by Union Carbide Nuclear Company for the U.S. Atomic Energy Commission.

(1) W. C. BEGGS, B. L. ROBINSON and R. W. FINK, *Phys. Rev.* **101**, 149 (1956).

(2) L. S. AUGUST, R. W. CAMPBELL and M. GOODRICH, *Bull. Amer. Phys. Soc.* **2**, #4 231 (1957).

(3) D. STROMINGER, J. M. HOLLANDER and G. T. SEABORG, *Revs. Mod. Phys.* **30**, 716 (1958).

(4) W. H. KELLEY and D. J. HOREN, *Bull. Amer. Phys. Soc.* **8**, #1 85 (1963).

(5) C. L. BURROS and R. L. BROOKSBANK, Method No. 2 21081 (7-1-52), *ORNL Master Analytical Manual*, TID 7015, Section 2.

(6) H. L. FINSTON, Private communication (1957).

A 500-μl aliquot of the Ba Cs solution was added to a separatory funnel, 2 ml of a 1 M sodium citrate-0 5 M nitric acid buffer solution added, and the volume made to 3 ml with water Three ml of a 0 05 M tetraphenyl boron in amyl acetate solution was added as an extractant, and the cesium was extracted into the organic phase by shaking for 30 sec After the phases had separated, the aqueous phase was drawn off and re-extracted with another 3 ml portion of the extractant The two organic phases were then combined, washed with 3 ml of buffer solution and then the cesium stripped with two, 2 ml portions of 3 N HCl The cesium fraction was made to volume in a 5 ml volumetric flask the original aqueous phase containing the barium was likewise made to volume in a 5 ml flask (The buffer wash and the organic phase after acid stripping were examined in every *experiment for residual activity The amount retained was in every case less than 1 per cent of the total*) One ml aliquots of the cesium and the barium dilutions were dried on 1 in watch glasses and used as sources for the 3 in 3 in NaI(Tl) γ-ray spectrometer equipped with a twenty-channel analyser In the ^{131}Cs source mount, the K X ray peak at 29 6 KeV was measured In addition, the total integral count above 50 KeV was obtained and in all cases found to be background or less This confirms the observation that ^{131}Cs decays only by electron capture and indicates the selectivity of the extraction method and the purity of the cesium product

The ^{131}Ba source mount was used to measure the X-ray region as well as the γ-rays from decay of ^{131}Ba The ratio of the K X-ray peak to the ^{131}Ba 496 KeV γ-ray was used as a test of the purity of the barium fraction This ratio was the same in all the separations made and was identical with that obtained from a spectrum obtained from a freshly separated exhaustively purified ^{131}Ba source *This also confirmed the selectivity of the extraction and the purity of the* ^{131}Ba *product*

MEASUREMENTS

The integrated peak area (P_t) obtained from the Cs^{131} K X-ray spectrum was used to calculate the disintegration rate of ^{131}Cs (A_2) using the expression

$$A_2 = \frac{P}{\Omega f K E_p A} \qquad (1)$$

where Ω solid angle at 9 3 cm (0 0373)
f fluorescence yield for Xe 0 84
K fraction of decay through K cap - 0 87$^{(7)}$
E_p peak efficiency - 1 00
A attenuation in crystal shielding 0 97

The activity of ^{131}Ba parent at the initial separation time (twelve or more days prior to the extraction) was then calculated in the usual manner

$$A_1 = \frac{(\lambda_2 - \lambda_1)A_2}{\lambda_2(e^{-\lambda_1 t} - e^{-\lambda_2 t})} \qquad (2)$$

where A_1 calculated ^{131}Ba parent disintegration rate at initial separation time
A_2 — observed ^{131}Cs daughter at extraction time
λ_1 — decay constant ^{131}Ba
λ_2 - decay constant ^{131}Cs
t - growth time of ^{131}Cs (i e, time between initial separation time and extraction)

The absolute number (N_γ) of 490 KeV γ-rays in the ^{131}Ba source was obtained from the integrated peak area in the γ-ray spectrum, using the published data of

---

(7) B R Joshi and G M Lewis, *Proc Phys Soc* **76**, 349 (1960)

LAZAR[8] This number (N_t) is related to the disintegration rate of ^{131}Ba (A_{Ba}) through the factor f

$$A_{Ba} = \frac{N_t}{f} \tag{3}$$

where f is the γ-branching in the decay of ^{131}Ba through the 496 KeV γ-ray N_t/f was corrected back to the initial separation time

$$A_1 = \frac{A_{Ba}}{e^{-\lambda_1 t}} = \frac{N_t}{f e^{-\lambda_1 t}} \tag{4}$$

or

$$f = \frac{N_t}{A_1 e^{-\lambda_1 t}} \tag{5}$$

where A_1 = calculated ^{131}Ba present at initial separation time
t decay time of ^{131}Ba (= growth time of ^{131}Cs)
λ_1 decay constant of ^{131}Ba

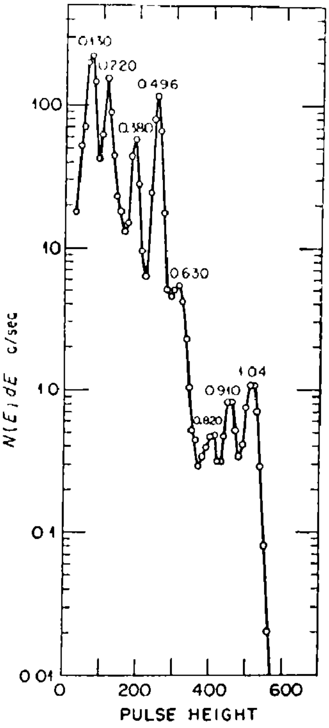


FIG 1 —γ-Ray spectrum of ^{131}Ba 20 KeV channel

f was obtained by substituting from Equation (2) the value for A_1 into Equation (5) From six determinations, each on a different day, f = 0 60 with a standard deviation of 0 03

Figure 1 shows the γ-ray spectrum of ^{131}Ba obtained by use of the 3 in × 3 in NaI(Tl) crystal and the twenty-channel analyser A considerably more active source was used to obtain these data than was used to measure the 0 496 KeV branching, since it was of interest here to determine intensities of the low abundant high energy γ-rays Successive graphical subtraction revealed γ-rays as indicated in Fig 1 Two different sources of ^{131}Ba of different age were used to obtain these spectra, in each of the solutions a slight amount of ^{133}Ba was present, as evidenced by the faint indication of a γ-photopeak at 370 KeV After decay of the ^{131}Ba had proceeded for a number of months, the ^{133}Ba contribution was corrected for by rerunning the γ-ray spectrum, matching the 370 KeV peak to a known ^{133}Ba γ-ray spectrum, drawing in this contribution to the ^{131}Ba spectrum, and subtracting Agreement between the γ-ray intensities in the two sources was within a few per cent The peak at 630 KeV is a composite of a true 600 KeV γ-ray photopeak and a coincident-sum peak of 630 KeV, which arises from coincidence summing between the 130 KeV and the 496 KeV γ-rays This was established (1) by measurement and comparison of the γ-ray spectrum obtained at 9 3 cm with that obtained at 20 cm, (2) by calculation of the contribution to the 630 KeV peak of summing in a manner similar to that described by Lazar (8) Both the previous techniques indicated the 630 KeV γ-ray photopeak to be due to coincidence summing Consequently, the observed photopeak intensities for both the 130 KeV and the 496 KeV γ-ray have been corrected for the slight loss at 9 3 cm of photopeak pulses due to summing These γ-ray intensities are listed in Table 1, together with previously reported values, the intensities measured in this work were obtained using the method of Lazar,(8) as previously described in the discussion of the ^{131}Ba determination Absolute intensities are also shown in Table 1 and were obtained by multiplying the relative intensities in Table 1 by the experimentally determined absolute intensity value of 0 60 for the 496 KeV γ-ray

---

[8] N H LAZAR, I R E Transactions of the Professional Group on Nuclear Science Vol NS-5 #3 138, December, 1958

TABLE 1 INTENSITIES OF γ-RAYS PRESENT IN ^{131}Ba DECAY

Energy, (MeV)	Relative intensities			γ's/dis Lyon
	August(2)	Beggs, *et al* (1)	Lyon	
0 130	0 73	0 56	0 47	0 28
0 220	0 55	0 42	0 46	0 28
0 380	0 36	0 28	0 26	0 16
0 496	1 00	1 00	1 00	0 60
0 600			0 053	0 032
0 630	0 03	0 09		
0 820		0 005	0 0057	0 0034
0 910		0 019	0 0016	0 0009
1 04		0 030	0 028	0 017

Inasmuch as the irradiation time of the material and the absolute activities of the ^{131}Ba ^{133}Ba could be calculated, the ratio of the pile neutron activation cross-sections $(\sigma_{130}/\sigma_{132})$ could be calculated The activity of the ^{133}Ba was calculated using the branching ratio of Langevin,(9) which has been verified in our laboratory and which assigns 75 per cent of the capture processes through the 370 KeV γ-ray The value obtained for this ratio $\sigma_{130}/\sigma_{132}$ is 1 36 ± 0 08 Beggs *et al* (1) have reported a value of

---

(9) M Langevin, *Ann Phys* **1**, 57 (1956)

1 2 ± 0 3 which was obtained using somewhat different assumptions regarding the decay schemes of ^{131}Ba and ^{133}Ba

The γ branchings for the ^{131}Ba γ-rays used by Beggs in the calculation of ^{131}Ba activity lead to a value about 10 per cent higher than that obtained by use of data in this report A larger difference arises in the ^{133}Ba activity calculations which was made by Beggs *et al* from a measurement of the 0 082 γ-ray and use of an earlier α_T value from Hayward *et al*$^{(10)}$ of 3 5 More recent measurements$^{(9,11)}$ indicate the α_T to be ~1 6 Measurements made in this laboratory confirm this latter figure In addition, these authors used 7 5 years as the half-life of ^{133}Ba Published data from ORNL indicates the half-life of ^{133}Ba to be 10 7 ± 0 2 yr$^{(12)}$

When one calculates the ratio $\sigma_{130}/\sigma_{132}$ by using the decay schemes and half-lives suggested in this paper, the value given by Beggs *et al* for the ratio $\sigma_{130}/\sigma_{132}$ is found to be 1 50 ± 0 39, this agrees well with our value of 1 36 ± 0 08

The half-lives of both ^{131}Ba and ^{131}Cs have been redetermined, ^{131}Ba by measurements on a high pressure gamma ionization chamber and ^{131}Cs by graphical integration of the *K* X-ray photopeak obtained by use of the 3 in × 3 in NaI(Tl) γ-ray spectrometer The half-life of ^{131}Ba is in agreement with previously published half-life of 12 0 days obtained at this laboratory$^{(13)}$

The half-life for ^{131}Cs was found to be 9 83 ± 0 28 days

DISCUSSION AND CONCLUSION

Nothing reported in this paper affects the level assignments made on the basis of coincidence and other nuclear measurements obtained in the past Consequently, no discussion of this subject is relevant The absolute γ-branchings as listed in Table 1 should now make it possible to assay accurately ^{131}Ba by γ-spectrometric methods The reactor neutron cross-section for the reaction ^{130}Ba(n, γ)^{131}Ba has been previously reported$^{(14)}$ as 8 8 barns Use of the ratio $\sigma_{130}/\sigma_{132}$ = 1 36 yields a value for ^{132}Ba(n, γ)^{133}Ba of 6 5 barns

(10) R W Hayward, D D Hoppes and H Ernst, *Phys Rev* **93**, 916 (1954)

(11) R K Gupta, S Jha, M C Joshi and B K Madan *Nuovo Cimento* **8**, 48 (1958)

(12) E I Wyatt S A Reynolds, T H Handley, W S Lyon and H A Parker *Nucl Sci Engng* **11**, 74 (1961)

(13) H W Wright, E I Wyatt, S A Reynolds, W S Lyon and T H Handley, *Nucl Sci Engng* **2**, 247 (1957)

(14) W S Lyon, *Nucl Sci Engng* **8**, 378 (1960)

J Inorg Nucl Chem, 1963 Vol 25 pp 1085 to 1087 Pergamon Press Ltd Printed in Northern Ireland

SPONTANEOUS FISSION HALF LIVES OF ^{254}Cf, ^{255}Fm, AND ^{250}Cf*

L PHILLIPS, R C GATTI, R BRANDT†‡ and S G THOMPSON
Lawrence Radiation Laboratory, University of California, Berkeley, California

(*Received* 8 *October* 1962, *in revised form* 19 *March* 1963)

Abstract—The remeasured spontaneous-fission half-life of ^{254}Cf is 60.5 ± 0.2 days The spontaneous-fission half-life of ^{255}Fm is determined to be $\left(1.0 \begin{smallmatrix} +0.6 \\ -0.3 \end{smallmatrix}\right) \times 10^4$ years The remeasured alpha-to-fission ratio in the decay of ^{250}Cf is (1330 ± 45) The remeasured electron-capture/β^--decay branching ratio in ^{254m}Es is (0.078 ± 0.006) per cent

INTRODUCTION

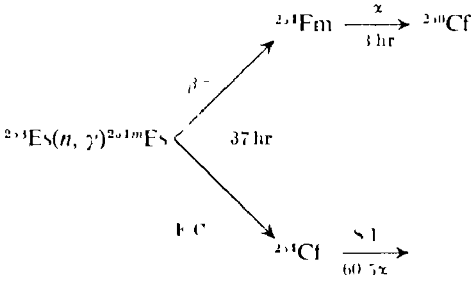
LARGER amounts of short-lived fermium, einsteinium and californium isotopes became available recently when they were separated from a mixture of curium isotopes that had been reirradiated in the Materials Testing Reactor at Idaho Falls, Idaho (MTR) This has made it possible to remeasure the spontaneous fission half-lives of ^{254}Cf and ^{250}Cf with greater precision

In addition, the spontaneous-fission half-life of ^{255}Fm was determined for the first time, and the ^{255}Fm α-half-life remeasured The electron capture branching ratio of metastable ^{254}Es was also remeasured

EXPERIMENTAL PROCEDURES

The ^{254}Cf source, which contained only 1.3% ^{250}Cf fission activity at the beginning of the ^{254}Cf fission half-life measurement, was prepared by irradiating isotopically pure ^{253}Es at the MTR Standard chemical procedures were used to purify and prepare the ^{254}Cf sample⁽¹⁾ The ^{254}Cf sample contained less than 0.05 per cent of ^{252}Cf fission activity

Neutron bombardment of ^{253}Es produces ^{254m}Es, which then decays to produce the daughters ^{254}Fm and ^{254}Cf, as shown below



(1)

The electron-capture branching ratio of ^{254m}Es was measured by separating ^{254}Fm and ^{254}Cf, which grew in from a pure sample of the ^{254m}Es parent, on a column of Dowex 50 × 12% cation-exchange resin by using ammonium α-hydroxy isobutyrate as the eluant The rates of α-emission and spontaneous fission in pure ^{255}Fm and ^{254}Cf fractions were measured in a windowless proportional counter

---

* This work was done under the auspices of the U S Atomic Energy Commission

† This author wishes to thank the Bundesministerium fur Atomkernenergie Bad Godesberg, Germany for financial support during this work

‡ Present address CERN, Geneva, Switzerland

⁽¹⁾ S G THOMPSON and M L MUGA, *Proceedings of the Second International Conference on Peaceful Uses of Atomic Energy, Geneva,* 1958 Paper P/825 United Nations (1959)

The ^{255}Fm sample was obtained by separating it from its parent ^{255}Es, which had been chemically separated from other elements The ^{255}Fm sample was counted for α-particles and fission fragments in two independent counting systems The decay of the ^{255}Fm fission activity was observed for about 100 hr (five half-lives)

The ^{250}Cf sample was obtained by separating it from an isotopically pure ^{254}Es sample, which decay as follows

$$^{254}\mathrm{Es} \xrightarrow[t_{1/2}\ \ 480\ \mathrm{days}]{\alpha} {}^{250}\mathrm{Bk} \xrightarrow[3\ 1\ \mathrm{hr}]{\beta} {}^{250}\mathrm{Cf} \xrightarrow[13\ \mathrm{years}]{\alpha} {}^{246}\mathrm{Cm} \tag{2}$$

The ^{250}Cf daughter had been growing into the parent sample for nearly one year before separation The ^{250}Cf fission-to-alpha ratio was measured in a windowless proportional counter

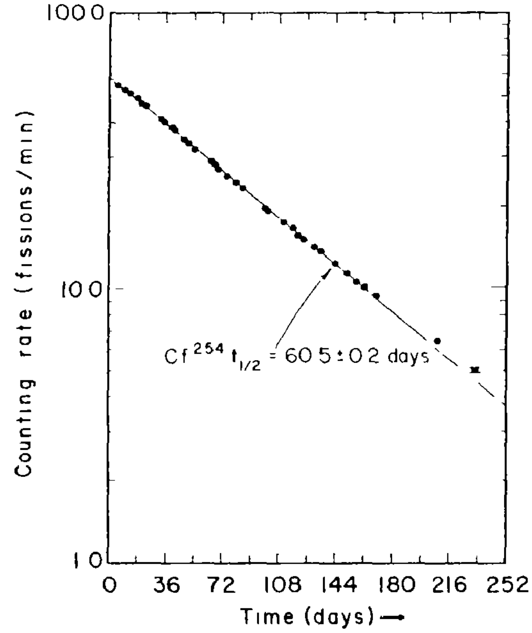


Fig 1 —Spontaneous-fission half-life of ^{254}Cf

RESULTS

The measured ^{255}Fm fission/alpha ratio is $(2\ 4^{+1\ 1}_{-0\ 6}) \times 10^{-7}$ The remeasured ^{255}Fm α-half-life is 19 9 ± 0 3 hr This agrees well with a recent measurement by Asaro(2) Our remeasured value for the ^{255}Fm α-half-life was used to calculate the ^{255}Fm spontaneous-fission half-life of $(1\ 0^{+0\ 6}_{-0\ 3}) \times 10^{4}$ years This value agrees well with Johansson's estimated value of 2×10^{4} years(3) It also fits smoothly into the spontaneous-fission systematics as developed by Swiatecki(4)

The new value for the electron-capture/β^{-}-decay branching ratio in ^{254m}Es is (0 078 ± 0 006) per cent

The experimental value for the ^{250}Cf alpha/fission ratio is (1330 ± 45) The ^{250}Cf spontaneous-fission half-life is $(1\ 73 \pm 0\ 06) \times 10^{4}$ years based on a 13 year α-half-life for ^{250}Cf(5)

(2) F Asaro, Lawrence Radiation Laboratory, private communication

(3) S A E Johansson, Lawrence Radiation Laboratory, private communication

(4) W J Swiatecki, *Phys Rev* **100**, 937 (1955)

(5) H Diamond, Argonne National Laboratory, private communication

A least-squares analysis of the data obtained by following the spontaneous-fission decay of ^{254}Cf over a period represented by four half-lives yields a value for the ^{254}Cf half-life of 60.5 ± 0.2 days. This result includes a correction for the spontaneous-fission activity (1.3 per cent) from a small amount of ^{250}Cf. The presence of ^{250}Cf in a sample of ^{254}Cf separated from ^{254m}Es is unavoidable, as may be seen from Equation (1). The correction involved measurement of the amount of ^{250}Cf present in the source by means of an α-particle-pulse-height analyser. From our value for the alpha/fission ratio of (1330 ± 45) we obtain a corrected least-squares value of 60.5 days for the ^{254}Cf spontaneous-fission half-life. Because of the uncertainty in the ^{250}Cf correction, an uncertainty of ±0.2 days is reported for the ^{254}Cf half-life. This is twice the standard deviation of ±0.1 day calculated directly by the least-squares analysis.

It might be interesting to note, that Burbidge *et al.* suggested that ^{254}Cf might have supplied the energy responsible for the exponential part of the light curves of Type-I supernovae which decays with a (55 ± 1)-day half-life,(6) since the hitherto-reported half-life for ^{254}Cf was (56.2 ± 0.7) days.(7) In a more recent study, Hoyle *et al.* suggest that this problem might be more complicated.(8) This suggestion is supported by the fact that the half-life of ^{254}Cf does not agree with the above-mentioned decay of the light curves of Type-I supernovae.

Acknowledgements—We wish to thank Dr. S. Fried, as well as F. McCarthy, J. Haley, J. Rees, and L. Gibson for their help in the experimental procedures. We are grateful to Drs. S. A. E. Johansson, W. J. Swiatecki and F. Asaro for helpful discussions.

(6) E. Burbidge, G. Burbidge, W. Fowler and F. Hoyle, *Revs. Mod. Phys.* **29**, 547 (1957).

(7) J. R. Huizenga and H. Diamond, *Phys. Rev.* **107**, 1087 (1957).

(8) F. Hoyle and W. A. Fowler, *Astrophys. J.* **132**, 582 (1960).

J. Inorg. Nucl. Chem. 1963, Vol. 25, pp. 1089 to 1091. Pergamon Press Ltd. Printed in Northern Ireland

DISCOVERY OF A NEW FERMIUM ISOTOPE*

R. C. GATTI, R. BRANDT,†‡ L. PHILLIPS and S. G. THOMPSON
Lawrence Radiation Laboratory, University of California, Berkeley, California

(*Received* 8 *October* 1962, *in revised form* 19 *March* 1963)

Abstract—A new spontaneous-fission activity has been observed in a fermium fraction separated from 120 mg of mixed curium isotopes which had been subjected to an integrated flux of 2.4 × 10^{22} neutrons per cm^2 at the Materials Testing Reactor, Idaho Falls, Idaho (MTR). A least-squares analysis of the spontaneous-fission decay data yielded a half-life of 10.8 days with a standard deviation of about $\left({}^{+2.2}_{-1.8}\right)$ days. An estimated half-life of $\left(11^{+10}_{-6}\right)$ days is reported here. The mass assignment is uncertain, but limited to *A* = 258 or 257.

IRRADIATION of curium isotopes in the high-flux MTR has produced transcurium isotopes as heavy as ^{256}Fm.⁽¹⁾ In recent years the amounts of transcurium isotopes have increased significantly. A study of decay systematics suggested that ^{257}Fm might have a half-life of the order of days or longer. It seemed interesting therefore to search for this isotope.

Chemical procedures

The irradiated curium target material was purified by standard chemical procedures.⁽²⁾ The fermium fraction separations and purification were completed about 12 days after the curium irradiation in the MTR. A separation factor of ~10^9 was obtained between fermium and einsteinium. The fermium sample used for the activity measurements contained ~100 α-decays per min of ^{253}Es. This source was prepared by electroplating on a platinum disk, and its α- and spontaneous-fission activity were studied for a period of several weeks.

ACTIVITY MEASUREMENTS

Results of the decay of the 11-day spontaneous-fission activity in the Fm fraction are presented in Fig. 1. Decay of the spontaneous-fission activity in the fermium fraction was followed with two independent counting systems. The first system involved a windowless proportional counter with a background of about 1 fission event/day. These results are denoted by *A* in Fig. 1. In the second system, spontaneous-fission events were detected by a 1 in. diam phosphorus-diffused solid-state detector and a multichannel pulse-height analyser with a negligible background. These results are denoted by *B* in Fig. 1.

The background and contributions from other spontaneous-fission activities are subtracted from the results shown in Fig. 1. The calculated contribution of the isotope ^{255}Fm to the spontaneous-fission activity of the sample⁽³⁾ amounted to 1.2 fission

---

* This work was done under the auspices of the U.S. Atomic Energy Commission.

† This author wishes to thank the Bundesministerium fur Atomkernenergie, Bad Godesberg, Germany for financial support during this work.

‡ Present address: CERN, Geneva, Switzerland.

⁽¹⁾ S. G. THOMPSON and M. L. MUGA, *Proceedings of the Second International Conference on Peaceful Uses of Atomic Energy, Geneva*, Paper P/825 United Nations (1959).

⁽²⁾ S. FRIED and H. SCHUMACHER, UCRL-10023, (1962).

⁽³⁾ L. PHILLIPS, R. C. GATTI, R. BRANDT and S. G. THOMPSON, *J. Inorg. Nucl. Chem.* **25**, 1085 (1963).

events per day at the start of counting This activity decayed with a half-life of 20 hr Contributions of the isotopes ^{254}Fm ($t_{1/2}$ 3 hr) and ^{253}Es ($t_{1/2}$ = 20 days) to the spontaneous-fission activity of the sample were negligible In addition, the sample contained a long-lived isotope ($t_{1/2}$ 3 months) with an activity of about 1 fission event per day

Because of the presence of 100 γ-decays per min of ^{253}Es in the Fm fraction, it was impossible to observe Fm alpha particles which might have had energies less than 6 7 MeV

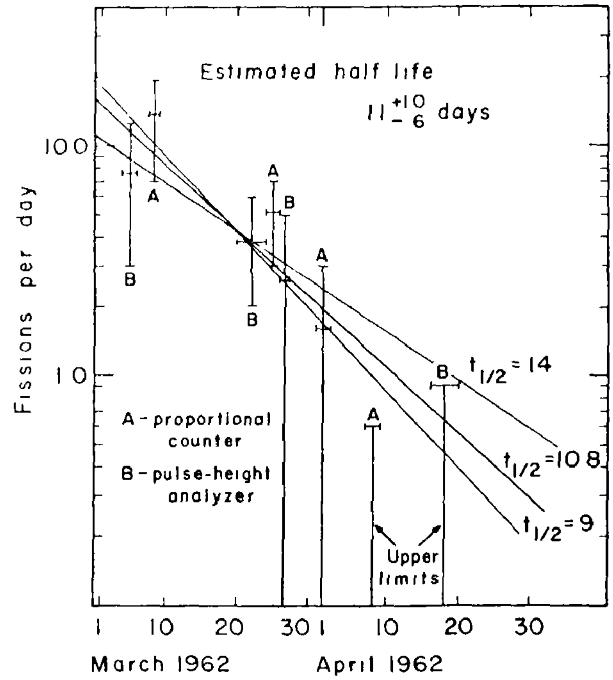


Fig 1 Decay of the new Fm isotope Approximately fifty events have been directly observed The activity is calculated from the observed events and the geometry factor Two different sets of counters were used The background is substracted

DISCUSSION

The assignment of the proton number $Z = 100$ to the 11-day fission activity is based on the following considerations It was observed only in the fermium fraction (The einsteinium fraction did not contain this activity—in any case, spontaneous-fission half-life systematics also indicate that an 11-day half-life is much too short for an einsteinium isotope) The chemical separation of the mendelevium and fermium fractions, which was repeated, also rules out the possibility that the eleven-day activity is a mendelevium isotope It is not possible that the eleven-day activity is the mendelevium daughter of a β-unstable fermium parent, because the last fermium-mendelevium chemical separation was completed twelve days after the end of the MTR bombardment If the half-life of the β-unstable fermium parent is less than two days, it would have decayed by this date If the postulated half-life of the β-unstable fermium parent is longer than two days, we would have observed the growth of the eleven-day daughter This consideration is also supported by an examination of cross-sections necessary for the formation of a fermium isotope of mass number 259, which is also predicted to be the first β-unstable fermium isotope It seems unlikely that the eleven-day fission activity would be an isomer of a known Fm isotope ^{254}Fm, ^{255}Fm or ^{256}Fm Therefore, the mass assignment is most likely A — 257 or 258

Acknowledgements —We wish to thank Dr S Fried, as well as F McCarthy, J Haley, L Gibson, J Rees, L White and A Fregulia for their help in the experimental procedures We are grateful to Drs S A E Johansson, W J Swiatecki, and F Asaro for helpful discussions

J Inorg Nucl Chem, 1963, Vol 25, pp 1093 to 1095 Pergamon Press Ltd Printed in Northern Ireland

ON THE SPECTRUM OF TRIPOSITIVE NEPTUNIUM IN SINGLE CRYSTALS OF LANTHANUM TRICHLORIDE

J B GRUBER
Department of Physics, University of California
Los Angeles 24, California

(*Received* 9 *January* 1963, *in revised form* 27 *February* 1963)

DURING the past several years the absorption and fluorescence spectra of Np^{3+}(5f^4) in LaCl$_3$ have been studied by the author at the Lawrence Radiation Laboratory in Berkeley, California, and the Institut fur technische Physik, der Technischen Hochschule, Darmstadt, Germany * While work is still progressing on the identification of all the crystalline Stark-split *J*-levels of Np^{3+} in LaCl$_3$, through continued experiments for the complete polarized fluorescence and Zeeman spectra and through a crystal-field splitting analysis for all *J*-levels, it seems reasonable to report at least the extent of some of the progress made so far since additional progress will be slower and tedious because of the complexity of the details of the spectrum

Using a Beckman IR-5 to cover the region below 2 0 μ and a Cary Model-14 to cover the region between 0 8 and 2 4 μ, the infrared absorption spectrum of Np^{3+} in LaCl$_3$ has been investigated from 600 to 12,000 cm^{-1} at 77°K Only the band widths of well defined peaks are recorded in Table 1 Greater resolutions and the absorption spectra at liquid helium temperature are needed to establish the accurate position of the structure appearing in the shoulders of the peaks reported in Table 1 Although plane polarized light was used in this study, the polarized absorption spectrum may be unambiguous only for the liquid helium data The three LaCl$_3$ single crystals used in this study weighed 2 0 grams each and contained approximately 1 0, 7 0 and 15 0 mg Np^{3+}(^{237}Np)

TABLE 1 —INFRA-RED ABSORPTION SPECTRUM OF Np^{3+} IN LaCl$_3$

	λ, Wavelength (μ)	Energy (cm^{-1})
1	2 58	3 880
2	2 53	3 950
3	2 48	4 030
4	1 40	7,140
5	1 35	7 410
6	1 20	8 330
7	1 18	8,470
8	1 12	8 930
9	1 09	9 170
10	1 07	9 346
11	1 00	10 000

---

*The author is particularly grateful for the helpful comments of Dr J G CONWAY of the Lawrence Radiation Laboratory, Berkeley, California and for the fruitful discussions and kind hospitality of Professor K H HELLWEGE of Darmstadt, Germany

Several fluorescence spectra have been photographed that indicate fluorescence takes place from several Stark-component levels in the near ultra-violet and visi regions of the spectrum At least one excited crystalline Stark-level has been established as a level from which fluorescence takes place to the ground-state level, $^5I_4$, and

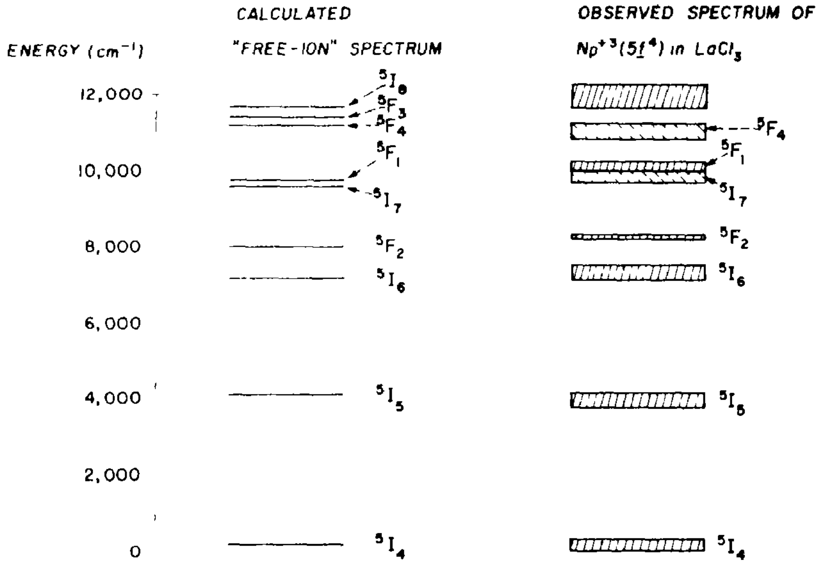


FIG 1 A comparison of the theoretical "free-ion" spectrum of $Np^{3+}(5f^4)$ with the observed spectrum of Np^{3+} in $LaCl_3$ The calculated spectrum based on a $\zeta = 2120$ cm^{-1}, and $F_2 = 235$ cm^{-1} is given on the left The observed spectrum is recorded on the right-hand side

to energy levels 4000, 7300 and 8350 cm^{-1} above the ground-state level The Stark-splitting of the $^5I_4$ level is about 200 cm^{-1} Since not all the Stark-components of some of these levels have as yet been identified, it is difficult to give more exact values for the centres of gravity

Since intermediate-coupling of the four $5f$ electrons plays such a large role in the discussion of the energy spectrum of $Np^{3+}(5f^4)$, it is impossible to establish the validity of the experimental J-level assignment using a simple Russell-Saunders-type calculation for the "free-ion" spectrum However, now that the coulombic and spin–orbit matrices for f^4 are available, one may calculate the intermediate-coupled "free-ion" spectrum directly (1 2 3) In order to see whether or not the "free-ion" spectrum agrees with the observed levels, the author chose as a preliminary calculation $\zeta = 2120$ cm^{-1}, $F_2 = 235$ cm^{-1} and the $5f$ hydrogenic Slater ratios $F_4/F_2 = 0.1422$ and $F_6/F_2 = 0.0161$ The choice of parameters for a preliminary calculation is not unreasonable if we consider the parameters used by other investigators for tripositive actinide spectra(4 5 6) See Table 2

(1) E F REILLY, *Phys Rev* **91**, 876 (1953)

(2) M H CROZIER and W A RUNCIMAN, *J Chem Phys* **35**, 1392 (1961)

(3) S HUFNER, *Z Phys* **164**, 257 (1961)

(4) J G CONWAY, J B GRUBER, E K HULET, R J MORROW and R G GUTMACHER, *J Chem Phys* **36**, 189 (1962)

(5) J B GRUBER and J G CONWAY, *J Chem Phys* **34**, 632 (1961)

(6) H LAMMERMANN and J G CONWAY, Lawrence Radiation Laboratory Report, UCRL-10257, Berkeley, California

The results from this calculation for all levels between 0.0 cm^{-1} and 12,000 cm^{-1} are given on the left-hand side in Fig. 1.* While additional spectral lines are observed between 11,000 and 12,000 cm^{-1} other than those assigned to a $J = 4$ level, there is still not enough experimental evidence to establish these lines as transitions to the crystalline Stark-components of the J-levels, $^5F_3$ and $^5I_8$, theoretically predicted. The experimental energy spectrum between 0.0 and 12,000 cm^{-1} is given on the right-hand side in Fig. 1. Any additional LSJ assignments will not be made until the Zeeman splitting is known and until the crystal-field-splitting analysis is complete. Likewise, it is difficult to obtain more refined Slater and spin-orbit parameters until more information is known regarding the experimental energy spectrum above 12,000 cm^{-1}.

TABLE 2.—THE SPIN–ORBIT AND F_2 PARAMETERS FOR CERTAIN TRIPOSITIVE ACTINIDE IONS

Ion	Configuration	ζ, (spin-orbit parameter) (cm^{-1})	F_2 (Slater parameter) (cm^{-1})	Reference
Cf^{3+}	$5f^9$	4000	300	4
Am^{3+}	$5f^6$	2600	225	5
Pu^{3+}	$5f^5$	2290	245	6
Np^{3+}	$5f^4$	2120	235	

---

*The author wishes to thank the UCLA Western Data Processing Center for the use of the IBM 7090 machine.

J. Inorg. Nucl. Chem. 1963, Vol. 25, pp. 1097 to 1098. Pergamon Press Ltd. Printed in Northern Ireland

THE SF$_5^-$ ANION

R. Tunder and B. Siegel
Laboratories Division, Aerospace Corporation, El Segundo, California

(*Received* 21 *February* 1963, *in revised form* 14 *March* 1963)

Abstract—Formation of a new type of anion, SF$_5^-$, is described. Salts of this anion with simple metal cations are not stable, but the tetramethylammonium salt is reasonably stable, exhibiting a small equilibrium dissociation pressure at room temperature. The tetramethylammonium salt of SF$_4$Cl$^-$ decomposes readily at this temperature. These salts of pentavalent sulphur were prepared by reacting liquid SF$_4$ with the corresponding tetramethylammonium fluoride or chloride.

Salts containing anions of the type SX$_5^-$ have not been previously reported. As a general rule the compounds in which second period elements such as sulphur exhibit maximum coordination numbers are the fluorides of these elements. Thus the SF$_5^-$ anion is the most probable anion of this type that should be capable of stable existence. However, while alkali metal salts of SeF$_5^-$ have been prepared by the reaction of SeF$_4$ with alkali fluorides,[1] the comparable reaction with SF$_4$ does not proceed. Bartlett and Robinson found that SF$_4$ will not complex with CsF.[2] We have confirmed the latter results, finding that SF$_4$ will not complex with CsF or BaF$_2$, even at temperatures down to −40°C. However, we have also found that SF$_4$ will react with (CH$_3$)$_4$NF to form an adduct whose stoichiometry approaches unity. In many complexing reactions reported for SF$_4$, it reacts with fluorides that are strong fluoride ion acceptors, the SF$_4$ transferring a fluoride ion to form salts of the SF$_3^+$ cation.[2] However, in the case of the SF$_4$–(CH$_3$)$_4$NF reaction, the opposite is clearly true and (CH$_3$)$_4$NF furnishes a fluoride ion to SF$_4$ to form (CH$_3$)$_4$N$^+$SF$_5^-$.

The evidence for the formation of an ionic complex when SF$_4$ is reacted with (CH$_3$)$_4$NF is substantial. Despite the magnitude of the SF$_4$ used, if this reagent is in excess the stoichiometry of the solid product which is formed is about 0.9 SF$_4$ 1.0 (CH$_3$)$_4$NF. This stoichiometry is obtained from both the increase in weight of the solid reactant and the quantity of SF$_4$ consumed. That no side reaction occurs is confirmed by the infra-red spectrum of the residual gas phase, which is simply that of SF$_4$. The complex can be conveniently dissociated almost quantitatively to the original reactants by heating. However at 25°C, there is only a small equilibrium pressure of 2–3 mm of SF$_4$ above the solid, as verified by the infra-red spectrum of the gas; upon standing for several days at ambient temperature the equilibrium pressure did not rise above this value. At 38°C this pressure rises to 7 mm and is only 19 mm at 60°C. The complex is also stable in solution and does not decompose when dissolved in dimethylformamide.

Despite the solubility in dimethylformamide the complex is not soluble in most organic solvents and reacts readily with water, nitromethane and monomethylformamide (with active hydrogens). This solubility in a solvent of high dielectric constant indicates the polarity of the complex. Further its infra-red spectrum exhibits the major absorption peaks characteristic of the (CH$_3$)$_4$N$^+$ cation (identical in its halide salts). The infra-red spectrum of the complex in dimethylformamide solution exhibits a new peak at 14 8 μ but the principal SF_4 peaks at 11 3-11 5 and 13 7 μ are absent from the spectrum This shift to lower frequencies is characteristic of anions formed by incorporation of fluorine ions into the structure of lower covalent fluorides of second period elements *

---

[1] E. E. Aynsley, R. D. Peacock and P. L. Robinson, *J. Chem. Soc.* 1231 (1952).
[2] N. Bartlett and P. L. Robinson, *J. Chem. Soc.* 3417 (1961).

Although the complex $(CH_3)_4NSF_5$ certainly represents a new electronic configuration for sulphur compounds, not many compounds of this type can be prepared Simple metal cations apparently cannot form stable salts of SF_5^-, and complex cations similar to $(CH_3)_4N$ are required, substitution of the bulky C_6H_5 group for one of the CH_3 groups in $(CH_3)_4N^+$ also prevents formation of a complex The reaction between SF_4 and $(CH_3)_4NCl$ leads to the formation of a very weak complex which decomposes readily at 25 C, thus the SF_4Cl^- anion is not very stable

Details of the complexing reactions are given below

EXPERIMENTAL

Preparations of reactants

Sulphur tetrafluoride, as obtained from the Du Pont Co , contained varying amounts of SiF_4 and SOF_2 It was purified by a method based on a suggestion by BARTLETT and ROBINSON(2) Equivalent amounts of SF_4 and BF_3 were reacted in a high vacuum line to form $SF_3^+BF_4^-$, from which the volatile impurities were distilled The complex was broken by addition of dry dioxane which displaces SF_4 and the latter was distilled at 60 C Purity was verified by inspection of the infra-red spectrum of the SF_4

Tetramethylammonium fluoride was prepared by reacting equivalent quantities of $(CH_3)_4NCl$ with KF in methanol The resulting $(CH_3)_4NF$ was isolated from the supernatant and recrystallized from isopropanol, the absence of a bifluoride impurity was verified by the absence of a bifluoride frequency in the infra-red spectrum of the product In previous experiments the $(CH_3)_4NF$ had been prepared by the reaction between $(CH_3)_4NOH$ and HF but this always led to the formation of a bifluoride impurity $C_6H_5(CH_3)_3NF$ was prepared by neutralization of the hydroxide with HF, but in this case the infra-red spectrum of the product indicated the absence of a bifluoride impurity

Complexing reactions

A large excess of SF_4 was distilled onto approximately one gram of dry $(CH_3)_4NF$ By maintaining the reaction at 40 to 20 C, the SF_4 was kept in the liquid state and $(CH_3)_4NF$ was essentially dissolved in excess SF_4 Detection of reaction was noted by distilling the excess SF_4 and reweighing the solid It was observed that a gradual increase in weight of the solid reactant occurred, which ceased after four hours At that point the increase in weight of the solid (originally $(CH_3)_4NF$) corresponded to approximately 0 9 SF_4 1 0 $(CH_3)_4NF$ That was indeed the stoicheiometry of the product was further verified by independent measurements of the SF_4 consumed during the reaction The infra-red spectrum of the SF_4 before and after the complexing reaction was essentially unchanged Together with the stoicheiometric determinations this verified that the complex was simply $(CH_3)_4NF\,(SF_4)_{0\,9}$

Under similar conditions there was no indication of complex formation between SF_4 and CsF or BaF_2 $(CH_3)_4NCl$ was also reacted with SF_4 but no indication of strong complexing occurred, some weight increase was observed but the product decomposed readily at room temperature, again releasing the SF_4 A complexing reaction between SF_4 and $C_6H_5(CH_3)_3NF$ was attempted, but there was no weight increase at all

Infra-red spectra were taken in the range 2 15 μ The spectrum of the solid product was taken in a KBr pellet and in dimethylformamide solution

* In the 2-15 micron range, there is one principal frequency at 9 7 μ for SiF_4,(3) In Na_2SiF_6, the peak has shifted to 13 9 μ (4) We have observed that $[(CH_3)_4N)]_2SiF_6$ also exhibits an absorption peak at 13 9 μ

(3) D C MCKEAN, *J Chem Phys* **24**, 1002 (1956)

(4) F A MILLER and C H WILLIAMS, *Analyt Chem* **24**, 1253 (1952)

J Inorg Nucl Chem 1963 Vol 25 pp 1099 to 1109 Pergamon Press Ltd Printed in Northern Ireland

CO-ORDINATION COMPLEXES OF NIOBIUM AND TANTALUM—I

COMPLEX FORMATION OF NIOBIUM AND TANTALUM PENTAHALIDES AND NIOBIUM (V) OXYCHLORIDE WITH ACETYLACETONE IN ALCOHOL SOLUTIONS AND FORMATION OF OXO-DICHLORO-ACETYLACETONATO NIOBIUM (V)*

C DJORDJEVIĆ and V KATOVIĆ
Laboratory of General and Inorganic Chemistry, Faculty of Science,
The University and Institute "Rudjer Bošković", Zagreb, Yugoslavia

(*Received* 15 *December* 1962, *in revised form* 12 *March* 1963)

Abstract—Complexes of the type $MX_2AcAc(OR)_2$, where M = Nb(V), Ta(V), X = Cl, Br, AcAc = acetylacetone, R = CH_3, C_2H_5 have been prepared from the metal pentahalides and acetylacetone in the parent alcoholic solutions They are stable crystalline substances, but in solutions in alcohols interactions with solvent molecules occur, as is evident from conductivity and molecular weight studies Powder X-ray diffraction photographs have shown that the methoxo chloro and bromo derivatives of niobium and tantalum are isomorphous, the analogous ethoxo complexes forming another isomorphous group Infra-red spectra have been analysed and a tentative assignment of some characteristic vibrational modes is given Metal–ligand vibrational modes appear at frequencies close to those in other metal acetylacetonates and metal alkoxides

Under similar experimental conditions, starting from $NbOCl_3$ and acetylacetone in methyl and ethyl alcohol solutions, complex derivatives of the same type, $NbCl_2AcAc(OR)_2$, have been isolated These results imply the unexpected solvolysis of the niobium–oxygen bond in alcohol solutions

A compound of the formula $[NbOCl_2AcAc]_x$ has been isolated from the reaction of $NbOCl_3$ with acetylacetone Infra-red spectrum of this oxo-dichloro-acetylacetonato niobium (V) reveals the presence of co-ordinated acetylacetone and the vibrational modes of the niobium–oxygen double bond Deuteration studies permitted the assignment of some bands

VERY few co-ordination complexes of niobium and tantalum have been reported so far and among them only some have been studied by modern experimental methods Earlier work[1,2] has shown that β-diketone complexes can be formed and some formulae were proposed, but further experimental evidence is necessary to confirm them However, the co-ordination numbers seven and eight have been well established in complex fluorides [3,4] It is to be expected that interesting stereochemical arrangements are present in co-ordination compounds of these two metals with different ligands More recently[5] alkoxides of Nb(V) and Ta(V) have been prepared

---

* Reported at the 7th International Conference on Co-ordination Chemistry, Stockholm and Uppsala (1962)

[1] A ROSENHEIM, E ROEHRICH, *Z Anorg Chem* **204**, 342 (1932)

[2] H FUNK, *Ber Dtsch Chem Ges* **67**, 1801 (1934)

[3] J L HOARD, *J Amer Chem Soc* **61**, 1252 (1939), M B WILLIAMS and J L HOARD, *Ibid* **64**, 1139 (1942)

[4] J L HOARD, W J MARTIN, M E SMITH, J F WHITNEY, *J Amer Chem Soc* **76**, 3820 (1954)

[5] D C BRADLEY, W WARDLAW and A WHITLEY, *J Chem Soc* 725 (1955), 1139 (1956), D C BRADLEY, B N CHAKRAVARTI and W WARDLAW, *Ibid*, 2381 (1956) 4439 (1956)

They are mainly dimeric, retaining in this way a co-ordination number six The hydrolysis of tantalum penta-alkoxides in solutions of the parent alcohols under controlled conditions leads to the formation of polymeric oxo-alkoxides, the polymeric structural models involving six-co-ordinated tantalum as well (6) Formation of 1 1 complexes of metal pentachlorides and bromides with diethylether,(7) dimethyl- and diethyl-sulphides has been reported(8) and a 1 2 complex has been observed with tetrahydrothiophene (8) Adducts of the metal pentahalides with pyridine,(9) and derivatives with aliphatic amines have also been described (10,11,12)

We have started an investigation of complex formation of niobium and tantalum pentahalides with different ligands, under various experimental conditions A group of complexes of the type $MX_2AcAc(OR)_2$ is discussed here The bromide derivatives of this series are new complexes The synthesis of analogous chloro compounds was reported earlier,(2) but no further studies were performed This group of complexes is particularly suitable for infra-red investigation, as it allows the study of spectral changes, dependent upon substitution of the metal, the halogen ion or the alkoxo group present

The complex formation by niobium (V) oxychloride studied under similar experimental conditions, has also been examined Cleavage of the niobium-oxygen bond in $NbOCl_3$ was observed in methyl and ethyl alcohol solutions, leading to the formation of complex derivatives of the type $NbCl_2AcAc(OR)_2$

So far, no complexes obtained by removing the chloride ion in the niobium oxychloride molecule have been reported in the literature Oxo-dichloro-acetylacetonato niobium (V) has been obtained in the course of these experiments and its properties are described The infra-red spectrum of this compound and its deuterium derivative are analysed and some characteristic vibrational frequencies are assigned A preliminary account of some results of these experiments has already been published (13)

EXPERIMENTAL

1 *Preparation of niobium and tantalum pentahalides*

$NbCl_5$ was prepared from freshly precipitated Nb_2O_5 by chlorination with chlorine in hexachlorobutadiene solution(14) The substance obtained was purified by sublimation *in vacuo*

$TaCl_5$ was prepared from freshly precipitated Ta_2O_5 and $AlCl_3$ (15) The mixture of stoichelometrical amounts of reactants was heated in an evacuated sealed tube at 400°C for 48 hr The $TaCl_5$ formed was separated by vacuum sublimation

$NbBr_5$ and $TaBr_5$ were prepared from the freshly precipitated metal oxides and $AlBr_3$ (15) It is necessary for the aluminium bromide to be in a large excess (about three times the stoicheiometrical amount) in order to prevent the formation of bromine The reaction mixture was heated in an evacuated sealed tube for 48 hr On slow cooling orange leaflets of $TaBr_5$ or red leaflets of $NbBr_5$ were obtained The bromides were purified by sublimation *in vacuo*

---

(6) D C BRADLEY and H HOLLOWAY, *Canad J Chem* **39**, 1818 (1961), **40**, 62 (1962)

(7) A COWLEY, F FAIRBROTHER and N SCOTT, *J Chem Soc* 3133 (1958)

(8) F FAIRBROTHER and J F NIXON, *J Chem Soc* 150 (1962)

(9) H C CLARK and H J EMELÉUS, *J Chem Soc* 190 (1958)

(10) P J H CARNELL and G W A FOWLES, *J Chem Soc* 4113 (1959)

(11) P J H CARNELL and G W A FOWLES, *J Less-Common Metals* **4**, 40 (1962)

(12) D C BRADLEY and I M THOMAS, *Canad J Chem* **40**, 449 (1962)

(13) C DJORDJEVIĆ and V KATOVIĆ, *Chem and Industr*, 411 (1963)

(14) T E AUSTIN, S Y TYREE, *J Inorg Nucl Chem* **14**, 141 (1960)

(15) M CHAIGNEAU, *C R Acad Sci, Paris* **243**, 957 (1956)

Preparation of niobium (V) oxychloride. $NbOCl_3$ was prepared from freshly precipitated Nb_2O_5(16) and $AlCl_3$.(17) By heating a mixture of 4 g Nb_2O_5 and 5 g $AlCl_3$ in an evacuated sealed tube on 240°C for 48 hr practically no $NbCl_5$ was formed, and the reaction product was $NbOCl_3$. On slow cooling large, needle-like white crystals can be obtained, and the rest of oxychloride is obtained by sublimation *in vacuo* at 10^{-4} mm Hg and 240°C.

Preparation of tantalum(V) *oxychloride.* $TaOCl_3$ was prepared by the method of Fairbrother *et al.*(18) by pyrolysis of tantalum pentachloride diethyl ether complex.

2. *Preparation of dichloro-acetylacetonato–dialkoxo-niobium (V) and tantalum (V)*

The complexes were prepared as described by Funk.(3) Vacuum sublimation was sometimes necessary to obtain them in a pure form. At 10^{-3} mm Hg the compounds can be easily sublimed between 130–150°C. At lower temperatures the process is too slow. (Found C, 25.9, H, 4.1, Cl, 21.5. $C_7H_{13}O_4Cl_2Nb$ requires C, 25.8, H, 4.0, Cl, 21.8. Found C, 20.7, H, 3.2, Cl, 16.3. $C_7H_{13}O_4Cl_2Ta$ requires C, 20.4, H, 3.2, Cl, 17.2. Found C, 29.5, H, 4.9, Cl, 19.6. $C_9H_{17}O_4Cl_2Nb$ requires C, 30.6, H, 4.8, Cl, 20.1. Found C, 24.0, H, 3.5, Cl, 15.7. $C_9H_{17}O_4Cl_2Ta$ requires C, 24.5, H, 3.8, Cl, 16.1%.) $NbCl_2AcAc(OR)_2$, where R = CH_3, C_2H_5 were also obtained by dissolving $NbOCl_3$ (0.7 g) in the parent alcohol (1 ml) and adding acetylacetone (0.4 ml) to this solution. Yellow crystals were formed almost immediately, treated as described above and sublimed at 10^{-3} mm Hg between 130–150°C. (Found C, 25.6, H, 4.1, Cl, 22.3, Nb, 28.6. $C_7H_{13}O_4Cl_2Nb$ requires C, 25.8, H, 4.0, Cl, 21.8, Nb, 28.5. Found C, 29.9, H, 4.8, Cl, 20.6, Nb, 24.8. $C_9H_{17}O_4Cl_2Nb$ requires C, 30.6, H, 4.8, Cl, 20.1, Nb, 26.4%.)

3. *Preparation of dibromo-acetylacetonato-dialkoxo-niobium (V) and tantalum (V)*

All these compounds were prepared by dissolving metal pentabromides (1 g) in parent alcohol (0.5 ml) and adding acetylacetone (0.2 ml) to the clear solution. The crystals obtained were filtered off, washed with a small amount of alcohol and petrol ether and dried *in vacuo*. They were sublimed at 10^{-3} mm Hg between 120 and 140°C. (Found C, 20.0, H, 3.2, Br, 38.6. $C_7H_{13}O_4Br_2Nb$ requires C, 20.4, H, 3.2, Br, 38.6. Found C, 17.7, H, 2.8, Br, 31.3. $C_7H_{13}O_4Br_2Ta$ requires C, 16.8, H, 2.6, Br, 31.8. Found C, 23.5, H, 4.2, Br, 36.5. $C_9H_{17}O_4Br_2Nb$ requires C, 24.4, H, 3.9, Br, 36.2. Found C, 20.3, H, 3.1, Br, 30.3. $C_9H_{17}O_4Br_2Ta$ requires C, 20.3, H, 3.2, Br, 30.2%.)

All the preparative work was done in a dry-box, because of the water sensitivity of the metal halides. AnalaR methanol and ethanol were purified and dried by standard procedures and AnalaR acetylacetone was dried by anhydrous sodium sulphate. The niobium and tantalum dihalogeno-acetylacetone-dialkoxo complexes obtained are much less sensitive to moisture than the metal pentahalides. In a desiccator they can be kept for months without decomposition.

4. *Preparation of oxo-dichloro-acetylacetonato niobium (V)*

To finely ground $NbOCl_3$ (0.5 g) acetylacetone (5 ml) was added. The reaction was carried out in a dry box with dry acetylacetone. The reaction mixture was shaken for a while and soon the solution became yellow and a yellow precipitate was formed. The substance was filtered off, washed with petrol ether and dried *in vacuo*. The compound does not melt, but decomposes above 200°C. It is not soluble in common solvents. (Found C, 21.8, H, 2.7, Cl, 24.8, Nb, 33.1. $C_5H_7O_3Cl_2Nb$ requires C, 21.5, H, 2.5, Cl, 25.4, Nb, 33.3%.)

Preparation of deuterated $[NbOCl_2AcAc]_x$. The deuterated complex was prepared as described above using deuterated acetylacetone, prepared as follows. 15 ml of freshly distilled acetylacetone was dried over anhydrous Na_2SO_4 and then shaken with 3 ml D_2O (99.9 per cent) for 1 hr. The mixture was left overnight, D_2O separated and acetylacetone dried again over Na_2SO_4.

5. *Analysis*

Niobium was determined gravimetrically and weighed in the form of the pentoxide. Chlorine and bromine were determined volumetrically with 0.1 M and 0.01 N $AgNO_3$ and dichlorofluorescein and eosin as indicators for chlorine and bromine respectively. Microanalyses for carbon and hydrogen were obtained.

(16) F. Fairbrother and J. B. Taylor, *J. Chem. Soc.* 4946 (1956).

(17) M. Chaigneau, *C.R. Acad. Sci., Paris* **743**, 957 (1956).

(18) F. Fairbrother, A. H. Cowley and N. Scott, *J. Less-Common Metals* **1**, 206 (1959).

6 *Physical measurements*

Molecular weight determinations Molecular weight of the complexes in the parent alcohol solution was determined ebullioscopically, by the method of Sucharda Bobranski All possible precautions were taken to exclude moisture, which causes hydrolysis of the compounds However, the pH of these carefully prepared solutions was always below seven, the acidity implying solvolysis The results obtained are presented in Table 1 They represent an average value obtained from three or more determinations in a concentration range of 0 02–0 04 molar solutions, the error amounting to about 5 per cent The concentration range was limited by the solubility of the complexes The determination of the molecular weight in a nonpolar solvent was not possible because of the insolubility of the compounds

7 *Conductivity measurements*

The conductivity of the parent 0 01 M alcohol solutions of the complexes was measured at 25° C All possible precautions were taken to exclude water The alcohols used were purified by the conventional methods (CH_3OH, $\kappa_{25^{\circ}}$ 3 14 10^{-6} C_2H_5OH, $\kappa_{25^{\circ}}$ 2 68 10^{-7}) The results of two separate runs involving alcohols of different initial purity, as checked by measuring the solvent conductivity, gave fairly consistent results for specific conductivities of the 0 01 M solutions, with the error given in Table 1 The corresponding molar conductivities are therefore of the order 159–167 for methyl and 46–64 for ethyl derivatives

Infra-red spectra The infra-red spectra were recorded in the region of 4000–400 cm^{-1}, on a Perkin Elmer Model 221, equipped with a grating and KBr prism Nujol and hexachlorobutadiene were used as mulling agents for different regions of the spectrum and the KBr pellet technique was employed to obtain frequencies covered by Nujol around 1400 cm^{-1} It was found that ionic exchange occurs to a certain extent in the KBr disks, and frequencies given in Table 1 are generally derived from nujol and hexachlorobutadiene spectra

Magnetic susceptibility Measurement of the magnetic susceptibility of all the compounds was performed and Gouy method was employed The complexes proved to be diamagnetic

X-ray examinations Powder diffraction photographs were taken by using nickel-filtered Cu K_α radiation with Philips powder camera ϕ 57 54 mm of specimens enclosed in a Lindemann glass capillary of 0 3 mm diam

RESULTS

In addition to the previously known chloro complexes of the type $MCl_2AcAc(OR)_2$, M – Nb,Ta, R CH_3,C_2H_5, the new corresponding bromo derivatives were prepared Niobium and tantalum dihalogeno-acetylacetonato-dialkoxo complexes are crystalline, stable substances with similar properties (see Table 1), not soluble in the common nonpolar organic solvents, but soluble in alcohols In water they undergo hydrolysis The complexes can be easily sublimed *in vacuo* and melt without decomposition The melting points of the methoxo and bromo-derivatives are generally higher than the melting points of the analogous ethoxo and chloro derivatives The colour of niobium and bromo derivatives is deeper than the colour of the related tantalum and chloro complexes The substitution of chloride by bromide ligand does not change the crystal structure Insertion of the ethoxo group however, changes the molecular arrangement in the solid state It was found that all the methoxo derivatives of this type are isomorphous, analogous ethoxo derivatives belonging to another isomorphous group

In the Table 1 molecular weight determination values are presented, obtained in solution of the parent alcohols In agreement with the conductivity data given in Table 1 and acidity of solutions, these results imply that the molecules of complexes undergo solvolysis and rearrangement occurs, involving probably an equilibrium between some new neutral and ionic species, formed by the attack of the solvent

In the Table 2 frequencies of the infra-red spectra of complexes $MX_2AcAc(OR)_2$

TABLE 1.—PHYSICAL PROPERTIES OF $MX_2AcAc(OR)_2$

Compound	Colour	Melting point	Molecular weight calcd	Molecular weight found in parent alcohols	Specific conductivity [Ω^{-1} cm^{-1}] at 25°C of 0.01 M solutions in parent alcohols
$NbCl_2AcAc(OCH_3)_2$	Yellow	127-129	325	112	$1.59 \pm 0.02 \times 10^{-3}$
$TaCl_2AcAc(OCH_3)_2$	Pale yellow	113-115	413	136	$1.60 \pm 0.01 \times 10^{-3}$
$NbBr_2AcAc(OCH_3)_2$	Dark yellow	111-113	414	130	$1.59 \pm 0.09 \times 10^{-3}$
$TaBr_2AcAc(OCH_3)_2$	Pale yellow	116-118 with decomp	502	142	$1.67 \pm 0.04 \times 10^{-3}$
$NbCl_2AcAc(OC_2H_5)_2$	Yellow	74-76	353	155	$5.0 \pm 0.1 \times 10^{-4}$
$TaCl_2AcAc(OC_2H_5)_2$	Pale yellow	63-66	441	200	$4.6 \pm 0.01 \times 10^{-4}$
$NbBr_2AcAc(OC_2H_5)_2$	Dark yellow	88-89	442	174	$6.4 \pm 0.5 \times 10^{-4}$
$TaBr_2AcAc(OC_2H_5)_2$	Pale brown	72-73	530	178	$6.0 \pm 0.4 \times 10^{-4}$

TABLE 2—INFRA-RED FREQUENCIES IN cm^{-1} OF $MX_2AcAc(OR)_2$

R = CH$_3$				R = C$_2$H$_5$			
X = Cl		X = Br		X = Cl		X = Br	
M = Nb	M = Ta	M = Nb	M = Ta	M = Nb	M = Ta	M = Nb	M = Ta
1560 *s*	1560 *s*	1560 *s*	1560 *s*	1561 *s*	1565 *s*	1550 *s*	1556 *s*
1530 *s*	1530 *s*	1528 *s*	1530 *s*	1530 *s*	1530 *s*	1535 *s*	1535 *s*
1425 *m*	1425 *m*	1423 *m*	1423 *m*	1420 *m*	1420 *m*	1425 *m*	1428 *m*
1335 *s*	1330 *s*	1330 *s*	1333 *s*	1341 *s*	1345 *s*	1335 *s*	1340 *s*
1288 *m*	1288 *m*	1288 *m*	1290 *m*	1288 *m*	1290 *m*	1290 *m*	1290 *m*
1145 *w*	1160 *w*	1145 *w*	1150 *w*	1143 *w*	1150 *w*	1140 *w*	1145 *w*
1110 *m*	1140 *w*	1110 *m*	1130 *sh*	1092 *m*	1096 *s*	1090 *w*	1093 *m*
1081 *s*	1105 *s*	1076 *s*	1100 *s*	1050 *s*	1068 *s*	1045 *s*	1063 *s*
1030 *m*	1030 *m*	1030 *m*	1032 *m*	1030 *m*	1031 *m*	1033 *sh*	1030 *m*
937 *w*	938 *w*	936 *w*	939 *w*	937 *w*	939 *w*	935 *s*	939 *s*
833 *w*	833 *w*	828 *w*	833 *w*	821 *w*	820 *w*	818 *w*	816 *w*
669 *s*	678 *s*	670 *s*	668 *s*	674 *s*	674 *s*	673 *s*	672 *s*
	672 *sh*		655 *sh*	653 *m*	653 *m*	651 *m*	652 *m*
	658 *sh*						
571 *s br*	554 *s br*	570 *s br*	553 *s br*	597 *s br*	588 *s br*	602 *s br*	588 *s br*
563 *sh*	537 *s*	562 *s*	535 *s*	546 *m*	548 *s*	544 *m*	548 *s*
548 *sh*		548 *sh*					
455 *s*	457 *s*	455 *s*	454 *s*	454 *s*	453 *s*	452 *s*	446 *s*
418 *w*	419 *w*	418 *w*	419 *w*	414 *w*	416 *w*	413 *w*	416 *w*

s—strong *m*—medium *w*—weak, *sh*—shoulder, *br*—broad are listed It was found, as expected, that the general shape of the spectrum differs very little on changing the metal or halogen ligand, the alkoxo group being of more influence The infra-red spectra of the complexes show the presence of the co-ordinated acetylacetone and vibrations of the alkoxo groups The position of the metal–oxygen vibrational modes associated with metal–ligand bond for alkoxo and acetylacetonato metal–oxygen bond, corresponds with the expected bond order, as found in the infra-red spectra of similar complexes

On treating $NbOCl_3$ with acetylacetone in methyl or ethyl alcohol an interesting phenomenon was observed The compounds formed and isolated under these conditions proved to be of the type $NbCl_2AcAc(OR)_2$ Therefore the solvolysis and breakage of the niobium–oxygen bond occurred, which was unexpected For this reason all possible experiments have been performed on the isolated complexes to confirm this conclusion On the basis of analysis, infra-red spectra and X-ray powder photographs, it has been established that dichloro-acetylacetonato–dialkoxo niobium (V) complexes are formed, identical with the complexes obtained when the preparation is started with niobium pentachloride

Oxo-dichloro-acetylacetonato niobium (V) was prepared from niobium (V) oxychloride It is a pale yellow crystalline substance, not soluble in common solvents In the Table 3 infra-red frequencies of this complex are listed in the region from 4000–400 cm^{-1} and tentative assignment is given The spectrum shows the presence of a co-ordinated acetylacetone molecule Deuteration studies have permitted the assignment of ring C—H modes, characteristic for $AcAc^-$ ligand The following bands have been found to shift on deuteration 3095 cm^{-1}, and 1185 cm^{-1} The corresponding C—D vibrational modes have been found at 2290 cm^{-1} and 928 cm^{-1} These bands are assigned as acetylacetone ring C—H stretching and in plane deformation vibration, respectively (19) The vibrational modes of the niobium–oxygen double bond are observed in the spectrum in the broad absorption range of 850–790 cm^{-1}, assigned by comparison with the spectra of niobium (V) oxychloride and chloro-acetylacetonato–alkoxo niobium (V) complexes The X-ray powder photograph shows that the complex is crystalline and not isomorphous with the parent oxychloride According to the magnetic susceptibility measurements $[NbOCl_2AcAc]_x$ is diamagnetic as expected for niobium (V), of d^0 electron configuration

The preliminary investigations have shown that the behaviour of tantalum oxychloride with acetylacetone is not identical to the behaviour of $NbOCl_3$ and under the same conditions the analogous tantalum (V) compound is not formed

DISCUSSION

Derivatives of niobium (V) and tantalum (V) pentahalides

The group of compounds of the type $MX_2AcAc(OR)_2$ represents an interesting system for studying the changes in the infra-red spectra on varying the metal the halogen and the alkoxo group present in the molecule X-ray powder photographs have shown that niobium and tantalum complexes of this type, possessing the same alkoxo group, are isomorphous and therefore on symmetry grounds the related vibrational modes can be compared The shifts of the corresponding frequencies can thus be ascribed to a certain extent to the alteration of the bond order of the bonds involved

---

(19) C Djordjević, J Lewis and R S Nyholm, *J Chem Soc* 4778 (1962)

The list of infra-red frequencies is given in Table 2 Tentative assignment of some bands can be made by comparison of the spectra with the well known spectra of metal acetylacetonates[20,21 22] and some infra-red data already reported for metal alkoxides [23 24] Two strong bands at 1560 and 1530 cm^{-1}, found at almost the same frequency in all complexes of this type, correspond with C O and C—C stretchings of a co-ordinated acetylacetone molecule The band ranging in different complexes from 1428 1420 cm^{-1} is a combination band predominantly the sym C—O stretch of the co-ordinated CO group and C H deformation, found in simple acetylacetonates at 10-30 cm^{-1} higher frequency Another CH_3-deformation vibration frequency, appearing from 1345 1330 cm^{-1} is also lower than in the simple acetylacetonates Small shifts of this band are observed on passing from methoxo to ethoxo derivatives, indicating that the alkoxo ligand is involved in this vibration as well In the region of 1300 1000 cm^{-1} a number of bands appear, arising from both organic ligands, belonging to different C–H and C-C vibrations A medium intensity single band is found at 1290 cm^{-1} in all the complexes of this type Complex absorption is then observed, many vibrational modes overlapping in a band shape characteristic for methoxo and ethoxo derivatives The maxima of this absorption region are metal sensitive, the one in tantalum complexes lying at a higher frequency They are also halogen and alkoxo group sensitive, the absorption being of a complex origin, involving probably a M O C vibrational mode of the metal and the alkoxo ligand Metal sensitive strong broad bands appear again in the region of 600–530 cm^{-1} According to the position of the corresponding M—O frequencies in the niobium and tantalum penta-ethoxides, at 556 and 571 cm^{-1} for Nb and Ta respectively,[23] these bands obviously include a M—O mode of the alkoxo ligand However, the absorption is complex, probably composed of several vibrational modes In tantalum complexes these bands appear at about 15 cm^{-1} lower frequency, in agreement with the mass effect of the metal atom The strong single band ranging in complexes from 457 to 446 cm^{-1} can be tentatively assigned as a M—O mode of the acetylacetonato ligand In this region no other strong absorption is expected from the ligand vibrations It is surprising that this band is not metal sensitive, except slightly in ethoxo bromides (shift of 6 cm^{-1}) This would imply a stronger bonded acetylacetone group in tantalum complexes, but to confirm this assumption, more evidence is necessary, in particular spectra in the lower frequency region Chloride and bromide ion have no influence on the infra-red spectra in the region examined, causing insignificant shifts in some ligand deformation vibrations

As shown by molecular weight and conductivity data, and indicated by acidity of the solutions, the complexes of the type $MX_2AcAc(OR)_2$ undergo solvolysis in the parent alcohol solutions. The study of this behaviour is not the concern of this paper However, a short discussion illustrating the experimental evidence is given In the

---

(20) L J Bellamy, *The Infra-red Spectra of Complex Molecules* Methuen, London (1958)

(21) K Nakamoto, P J McCarthy and A E Martell, *J Amer Chem Soc* **83**, 1272 (1961), and references given there

(22) C Djordjević, *Spectrochim Acta* **17**, 448 (1961)

(23) C G Baraclough, D C Bradley, J Lewis and I M Thomas, *J Chem Soc* 2601 (1961)

(24) A P Simonov, D N Šigorin, T V Talalaeva, *Dokl Akad Nauk SSSR*, **141**, 665 (1961)

concentration range studied, which was limited by the solubility of the substances, consistent molecular weight values were found and reproducible specific conductivities were obtained. It appears therefore that in alcohol solution an equilibrium between different neutral and ionic species is present.(25) The solvent interaction may, for example, involve reactions of the type shown by Equations (1) and (2).

$$\begin{tikzcd} NbX_2AcAc(OR)_2 \arrow[r, shift left, "ROH"] & NbX_2(OR)_3 + H^+ + AcAc \arrow[l, shift left] \arrow[d, shift left] \\ & \tfrac{1}{2}Nb_2X_4(OR)_6 \arrow[u, shift left] \end{tikzcd} \qquad (1)$$

$$\begin{tikzcd} NbX_2AcAc(OR)_2 \arrow[r, shift left, "ROH"] & NbXAcAc(OR)_3 + H^+ + X^- \arrow[l, shift left] \arrow[d, shift left] \\ & NbAcAc(OR)_4 + H^+ + X^- \arrow[u, shift left] \end{tikzcd} \qquad (2)$$

Numbers obtained by molecular weight determination reflect then an average value, dependent upon the equilibrium concentration of the neutral and ionic species formed by solvolysis.

Derivatives of niobium (V) oxychloride

In general niobium has a much stronger tendency than tantalum to form oxy-compounds. Therefore the most striking feature of the results of this investigation is the behaviour of $NbOCl_3$ in methanol and ethanol solutions. The reaction may be described by the general equation

$$NbOCl_3 + HAcAc + ROH \rightarrow NbCl_2AcAc(OR)_2 + H^+ + Cl^- + H_2O$$

The polymeric chains, existing in the parent niobium (V) oxychloride(26) are therefore broken in alcohol solutions, the solvolysis yielding the same reaction product as in the case of niobium pentachloride.

Action of acetylacetone on powdered $NbOCl_3$ at room temperature yields a compound of the formula $NbOCl_2AcAc$. One of the chloride ions can therefore be easily removed with acetylacetone. The insolubility, as well as decomposition without melting, imply that the complex formed is of polymeric nature, the solid state structure involving chlorine and possibly oxygen bridges, as found in the oxychloride itself. The formula would be thus better represented as $[NbOCl_2AcAc]_x$. Owing to insolubility it was not possible to determine the molecular weight of the complex.

In Table 3 the infra-red frequencies of oxo-dichloro-acetylacetonato complex and its deutero-acetylacetonato parallel are listed. Characteristic bands can be assigned on comparison of this spectrum with the spectra of $NbOCl_3$, $NbX_2AcAc(OR)_2$, and by reference to the well known spectra of metal acetylacetonates.(21–28) Sym and asym C—O stretchings are placed at slightly lower frequencies, implying a lower C—O bond order. This should be associated with stronger Nb—O ($AcAc^-$) bonds. The position of the Nb—O stretching mode frequency at 470 cm^{-1} is in agreement with such a conclusion, if compared with the related band located in $NbCl_2AcAc(OR)_2$ at 455 cm^{-1}. The deuterium shifts for ring C—H stretching and deformation modes ($\nu_H/\nu_D = 0.740$, and $\nu_H/\nu_D = 0.783$, respectively) are of the order found in cupric

---

(26) A. M. El-Aggan, D. C. Bradley and W. Wardlaw, *J. Chem. Soc.* 4643 (1958).

(28) D. E. Sands, A. Zalkin and R. E. Elson, *Acta Cryst.* **12**, 21 (1959).

TABLE 3.—INFRA-RED SPECTRUM OF $[NbOCl_2AcAc]_x$ IN cm^{-1}

$NbOCl_2(CH_3COCHCOCH_3)$	$NbOCl_2(CH_3COCDCOCH_3)$	Probably assignment
3095 *w*		Ring C—H stretch
2965 *vw*	2965 *vw*	Methyl C—H stretch
2925 *m*	2925	
	2290 *m*	Ring C—D stretch
1550	1550	C—C and C—O stretch
1540 *s*	1540 *s*	
	1515 *sh*	
1420 *m*	1420	C—O stretch +C—H def
	1410 *sh*	
1365 *m*	1365 *m*	CH_3 def and C—C stretch
1305 *s*	1295 *s*	
1185 *vw*		Ring C—H in plane def
1170 *vw*	1170 *vw*	
1033 *m*	1030 *m*	
1013 *sh*	1010 *sh*	
940 *m*	940 *m*	
-	928 *m*	Ring C—D in plane def
850 *sh*		Nb—O mode, and Some other deuterium sensitive modes
835 *sh*	830 *sh*	
820 *s*	820 *s*	
800 *s*	800 *sh*	
678 *m*	679 *m*	
	669 *sh*	
	660 *sh*	
646 *m*	647 *m*	
556 *m*	556 *m*	
530 *m*	527 *m*	
470 *s*	470 *s*	Nb—O stretch
420 *w*	420 *vw*	

s—strong, *m*—medium, *w*—weak, *vw*—very weak, *sh*—shoulder

acetylacetonate.[(19)] The corresponding out of plane C—H deformation is expected in the region around 780 cm^{-1}, where it cannot be detected in this spectrum because of the strong absorption including the niobium–oxygen double bond vibration. However, additional bands are found in the spectrum of the deuterated complex at 669 and 660 cm^{-1}. A characteristic feature of the $[NbOCl_2AcAc]_x$ spectrum is the strong broad band with the joint maxima at 820 cm^{-1} and 800 cm^{-1}, not present in the spectra of metal acetylacetonates, nor in the spectra of chloro-acetylacetonatoalkoxo complexes. This band can be therefore assigned as a combination band including a niobium–oxygen double bond vibrational mode. The corresponding peak appears in $NbOCl_3$ at 770 cm^{-1}, as a broad band too, but covering a shorter wave length range. It has been shown that the niobium (V) oxychloride structure is polymeric,[(26)] the planar Nb_2Cl_6 groups jointed into infinite chains by Nb—O—Nb bonds. Therefore the infra-red frequency at 770 cm^{-1} represents a vibrational mode of a lower bond order double bond. In oxo-dichloro-acetylacetonato complex the corresponding band covers the region between 850–790 cm^{-1}, with a maximum at 820 and 800 cm^{-1}. In the deuterated complex the maximum at 800 cm^{-1} is not resolved and the absorption range is contracted, indicating in this way the complexity of the vibration, composed of several modes, some of them deuterium sensitive. It is therefore not possible to determine the exact shift of the corresponding frequency on passing from the oxychloride to oxo-dichloro-acetylacetonato complex and to derive from it exact conclusions about the alteration of bond character However, the pronounced difference of about 50 cm^{-1} on passing from $NbOCl_3$ to $[NbOCl_2AcAc]_x$ obviously indicates a higher double bond character of this bond in the acetylacetonato complex A frequency in the range 1100 900 cm^{-1} was assigned as a metal-oxygen double bond vibrational stretching mode for a number of compounds containing Ti=O, V- O, Mo O and Cr O bonds (27) Compared with these values Nb O band appears at a lower frequency, in accordance with the Nb—O – Nb type of bridging structure

Acknowledgements- The authors are grateful to Prof R S **Nyholm**, F R S , Prof D C **Bradley** and Prof D **Grdenić** for discussion They also thank B **Korpar** and O **Hadžija** for microanalyses and T **Magjer** for technical assistance in recording the spectra

(27) C G **Brraclough** J **Lewis** and R S **Nyholm**, *J Chem Soc* 3552 (1959)

J Inorg Nucl Chem, 1963, Vol 25 pp 1111 to 1113 Pergamon Press Ltd Printed in Northern Ireland

COMPLEXES OF URANYL ION WITH *DIMETHYL*-FORMAMIDE AND SEMICARBAZIDE*†

N A FRIGERIO and R F COLEY
Division of Biological and Medical Research Argonne National Laboratory
Argonne, Illinois
and
St Procopius College, Lisle, Illinois

(*Received* 15 *October* 1962 *in revised form* 8 *March* 1963)

RECENT conductivity measurements of hydrated uranyl ion in various solvents⁽¹⁾ have indicated complete replacement of the water molecules of the first solvation shell by such Lewis bases as formamide, much in the manner of the well known ammonia, ether, ketone and phosphate complexes In the synthesis of organo-uranium compounds from Group I and II organo-metallics, a high-boiling, weakly basic, anhydrous, reducing solvent system was required Preliminary experiments showed dimethylformamide, sometimes in the presence of semicarbazide, to be the solvent system of choice The water molecules introduced with hydrated uranyl salts, however reacted so quickly with the organometallics that little or no organo-uranium compound was formed Anhydrous uranyl nitrate⁽²⁾ proved difficult to prepare and store and, further, reacted so violently with the solvent that extensive side reactions occurred As an alternative we have been able to prepare and isolate some crystalline complex uranyl salts that have proven very useful synthetic intermediates

Twenty-five grammes of $[UO_2(H_2O)_2](CH_3COO)_2$ refluxed 10 min with 25 g of dimethylformamide, $HCON(CH_3)_2$, and cooled to 0°C yielded a heavy crop of dense yellow rhombic crystals of uranyl dimethylformamide acetate Refractometry of the solution remaining showed that considerable water had been liberated during the reaction The product was recrystallized from boiling $HCON(CH_3)_2$, washed with cold acetone, and dried at 65°C to constant weight The bright yellow crystals decomposed above 110°C The compound was soluble in dimethylformamide, water, glacial acetic acid, acetone, methanol, ethanol and propanol-2 (Found U, 51·61, C, 18·29, H, 2·87, N, 3·01, O, 24·22 Calc for $[UO_2(HCON(CH_3)_2)_2](CH_3COO)_2$ U, 51·67, C, 18·23, H, 2·84, N, 3·04, O, 24·28 %)

Similarly, 30 g $[UO_2(H_2O)_6](NO_3)_2$ refluxed for 10 min with 29 g $HCON(CH_3)_2$, cooled to 0°C, filtered, washed with cold acetone, and dried at 120°C, yielded 24 g (74 per cent) crude uranyl di(dimethylformamide) nitrate Recrystallization from boiling dimethylformamide yielded bright yellow crystals melting at 176·7–177·3°C (Found U, 44·09, C, 13·43, H, 2·67, N, 10·29, O, 29·52 Calc for $[UO_2(HCON(CH_3)_2)_2](NO_3)_2$ U, 44·06, C, 13·33, H, 2·61, N, 10·37, O, 29·61 %) The compound, while soluble in water, glacial acetic, acetone, methanol and propanol-2, was less so than $[UO_2(H_2O)_6](NO_3)_2$, and, unlike the latter, was completely insoluble in ether Aqueous solutions of these compounds gave refractive indices identical to those of known solutions of the hydrated salts plus 2 moles of dimethyl formamide per mole of salt This suggested that the dimethyl formamide was bound to the uranyl ion but otherwise unchanged Similarly, chemical tests on aqueous solutions were positive for acetate or nitrate ions and infrared spectra confirmed the presence of unre-arranged dimethyl formamide and acetate or nitrate ions

---

* Work performed under the auspices of the U S Atomic Energy Commission and supported in part by a National Foundation Undergraduate Research Grant

† Taken, in part, from the B S Dissertation of Ronald F Coley, St Procopius College, 1962

⁽¹⁾ B JEZOWSKA-TRZEBIATOWSKA and M CHMIELOWSKA, *J Inorg Nucl Chem* **20**, 106 (1961)

⁽²⁾ G GIBSON and J J KATZ, *J Amer Chem Soc* **73**, 5436 (1951)

Ultra-violet and visible spectra of the uranyl di(dimethylformamide) nitrate in water were identical with those of uranyl hexaaquo nitrate in water or ether⁽²⁾ Spectra of the uranyl di(dimethylformamide) nitrate in either ether or dimethylformamide, however, were identical with those of anhydrous uranyl nitrate in ether⁽²⁾ This suggests that ether and dimethylformamide interact with the same orbitals of the uranyl ion, but that the latter ligand is much more firmly bound

The Lewis base semicarbazide, although capable of complexing uranyl ion, failed to replace all of the waters in the solvation shell A bright yellow solution was obtained after heating 0 01 mole of any of the uranyl salts listed below and 0 10 mole of semicarbazide hydrochloride in 25 ml of water for 10 min The solution was cooled to 0°C, and 5 ml pyridine and 25 ml ether were added The resultant bright yellow monoclinic crystals were collected by suction filtration, recrystallized from boiling water, washed with cold ether, and dried at 120 C to yield 0 0093 mole (93 per cent) of $[UO_2(H_2O)_2(NH_2CONHNH_2)_3]Cl_2$, melting point 215°C with decomposition (Found U, 39 74, C, 6 78, H, 3 40, N, 21 28, Cl, 11 76, O, 17 04 Calc for $[UO_2(H_2O)_2(NH_2CONHNH_2)_3]Cl_2$ U, 39 53, C, 6 00, H, 3 18, N, 20 93, Cl, 11 76, O, 18 60%)

The same compound, uranyl diaquo trisemicarbazide chloride, was obtained using $[UO_2(H_2O)_6](NO_3)_2$, $[UO_2(HCON(CH_3)_2)_2](NO_3)_2$, $[UO_2(H_2O)_3]Cl_2$, or $[UO_2(H_2O)_2](CH_3COO)_2$ This indicated that the chloride salt was either less soluble or more readily formed than the nitrate or acetate The complex chloride was soluble in cold water or hot glacial acetic acid, but insoluble in hot or cold propanol-2, ether, methanol or acetone The complex chloride was formed in the absence of pyridine also, but in much lower yield and far more slowly Since bases such as pyridine can act to yield free semicarbazide from its hydrochloride,⁽³⁾ it would appear that the Lewis base semicarbazide, and not the semicarbazidonium ion, is the reactive species

Addition of excess silver nitrate to an aqueous solution of the complex salt yielded two moles of silver chloride per mole of salt, indicating that the chloride of the complex salt existed as a simple anion

The fact that repeated recrystallization from boiling water failed to increase the number of bound waters is consonant with the spectral evidence from the di-dimethylformamide, hexaaquo and ether complexes⁽²⁾ This is also in agreement with the observation that attempts to remove the waters from $[UO_2(H_2O)_2](NO_3)_2$ result only in decomposition to U_3O_8 These results suggest that two of the available hydration sites of uranyl ion are of markedly higher energy than the remaining ones

Attempts to prepare uranyl complexes containing both semicarbazide and dimethylformamide failed Refluxing $[UO_2(H_2O)_3]Cl_2$ and semicarbazide hydrochloride in dimethylformamide resulted only in the evolution of ammonia, precipitation of UO_2 and formation of $NH_2CONHNHCONH_2$ (biurea) The latter was

---

(3) L F AUDRIETH, *J Amer Chem Soc* **52**, 1250 (1930)

identified from its melting point (259°C, reported(5) 257°C), complete lack of absorption in the ultra-violet, CONH (3170, 1620 and 1580 cm^{-1}) and NH_2 (1090, 980 cm^{-1}) bands in the infrared, and elemental analysis (Found: C, 20.24, H, 4.92, N, 45.84, Cl, 0.00, ash, 0.00. Calc. for $NH_2CONHNHCONH_2$: C, 20.34, H, 5.12, N, 47.44%.)

Although the same compound could be obtained by simple refluxing of semicarbazide in dimethylformamide, the reaction required many hours, rather than a few minutes, and liberated hydrazine, rather than ammonia. Hence, the formation of biurea in the presence of uranyl ion must be due to oxidation of the semicarbazide to biurea(4) with the resultant production of ammonia and a very reactive and finely divided form of UO_2. The latter was identified by its X-ray diffraction pattern, conversion to U_3O_8 at 750°C and solution in sulphuric acid to give the green uranous ion.

In addition to their possible interest as complexes the uranyl dimethylformamide proved useful, as anticipated, in permitting organometallic syntheses impossible with the aquo salts. Thus, reaction of uranyl di(dimethylformamide) nitrate with lithium phthalocyanine in dry dimethylformamide proceeded smoothly and nearly quantitatively, to uranyl phthalocyanine. The same reaction with uranyl hexaaquo nitrate gave only the hydrolysis product, dihydrogen phthalocyanine.

Acknowledgement—One of us (R. F. C.) wishes to thank the National Science Foundation Undergraduate Research Participation Program for financial support.

(4) P. F. Wiley, *J. Amer. Chem. Soc.* **76**, 5176 (1954).

( ) J. Beilstein, Handbuch der Organischen Chemie 3, 116, I 56, II 95, III 229. Springer-Verlag, Berlin (1919).

J Inorg Nucl Chem , 1963, Vol 25, pp 1115 to 1118 Pergamon Press Ltd Printed in Northern Ireland

ON MOLYBDENUM AND TUNGSTEN DIOXIDES AND DIOXYDICHLORIDES

F Zado
Department of Structural and Inorganic Chemistry,
Institute "Rudjer Bošković", Zagreb, Yugoslavia

(*Received* 10 *August* 1962, *in revised form* 28 *January* 1963)

Abstract—A simple method for the laboratory preparation of molybdenum and tungsten (IV) oxides is described The reaction is carried out by reduction of molybdenum (VI) and tungsten (VI) oxides with gaseous ammonia Dioxydichlorides of molybdenum and tungsten are obtained by partial chlorination of their (VI) oxides with carbon tetrachloride vapour in an atmosphere of oxygen Temperatures for the oxidation of molybdenum (IV) and tungsten (IV) oxides are determined by means of differential thermal analysis

GROWING interest in the coordination chemistry of molybdenum and tungsten made us devise simple quick methods for the laboratory preparation of their (IV) oxides and dioxydichlorides, which are, starting materials for the preparation of molybdenum and tungsten complexes

Molybdenum (IV) and tungsten (IV) oxides Although there are many published preparations of molybdenum (IV) and tungsten (IV) oxides, most of them were found unsuitable, requiring a lot of time, and some could not be reproduced at all

Amongst a number of reducing agents which have been used for the reduction of molybdenum (VI) and tungsten (VI) oxides to the corresponding (IV) oxides, we have chosen ammonia gas for several reasons it is safe to handle, with excellent reducing properties at relatively low temperatures, comparable with those of hydrogen According to earlier data(1,2,3) reduction of molybdenum (VI) to molybdenum (IV) oxide by ammonia, can be carried out in a melt of ammonia molybdate, ammonium chloride and potash (or boric acid—in order to facilitate melting), or by gaseous ammonia (4,5)

Earlier data on the reaction between ammonia and tungsten (VI) oxide do not mention tungsten (IV) oxide as a product

Molybdenum and tungsten dioxydichlorides Molybdenum dioxydichloride can be considered as the final product of the oxidation of different molybdenum chlorides and oxychlorides(6) but this is not the case with tungsten(7,8) where oxidation proceeds to tungsten oxytetrachloride only One of the best chlorinating agents for metallic oxides, is carbon tetrachloride, but its action on molybdenum (VI) and tungsten (VI)

---

(1) J J Berzelius, *Pogg Ann* **6**, 335 (1826)
(2) W Muthmann, *Lieb Ann* **238**, 116 (1887)
(3) M Guichard, *C R Acad Sci , Paris* **125**, 105 (1897)
(4) D K Tuttle, *Lieb Ann* **101**, 287 (1857)
(5) C Rammelsberg, *J Prak Chem* **97**, 174 (1866)
(6) C W Blomstrand, *J Prak Chem* **71**, 466 (1857)
(7) W Forcher, *J Prak Chem* **86**, 234 (1862)
(8) C W Blomstrand, *J Prak Chem* **89**, 238 (1863)

oxides leads to the formation of a mixture of different molybdenum or tungsten chlorides and oxychlorides (9 10 11)

RESULTS AND DISCUSSIONS

Molybdenum (IV) *and tungsten* (IV) *oxides*

Contrary to uranium (VI) oxide, molybdenum (VI) oxide and tungsten (VI) oxide are readily reduced by means of gaseous ammonia to metallic molybdenum and tungsten (12) Therefore a careful selection of reaction conditions, temperature, flow-rate of ammonia, and duration of reaction is required Rapidity of preparation and maximum yield of reaction products on the laboratory scale were desirable Therefore high flow-rates and temperature were necessary The reduction, carried out at first in a horizontal furnace, showed considerable differences in the molybdenum or tungsten content of the products, amounting to 0 35 per cent between the front and rear of the boat in which the oxides were placed Heating molybdenum (VI) and tungsten (VI) oxides in a vertical position (method of the "boiling zone"(13)) was more promising The oxides were placed in a porcelain crucible, kept in the reaction tube

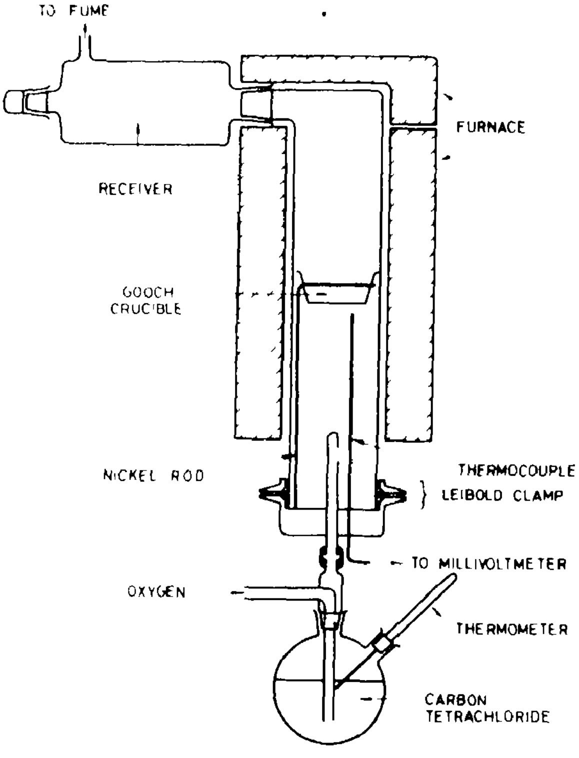


FIG 1

---

(9) C W WATTS, C A BELL, *J Chem Soc* **33**, 443 (1878)

(10) H QUANTIN, *C R Acad Sci, Paris* **104**, 223 (1887)

(11) P CAMBOULIVES, *C R Acad Sci, Paris* **150**, 175 (1910)

(12) F WOHLER, *Lieb Ann* **73**, 198 (1850)

(13) A W NOVOSEKOVA, K N SERMENKO *Zh Neorg Khimii*, **3**, 2213 (1958)

of a vertical furnace Reduction was then uniform, except when oxide layer exceeded 5 mm This difficulty was eliminated by using a Gooch crucible (holes about 0 5 mm) The amount of oxides to be reduced varied between 15–20 g, requiring 30–90 min for completion

In Fig 1 the form of the apparatus used for the preparation of molybdenum (IV) and tungsten (IV) oxides is shown It is important to mention that the apparatus was modified in some details commercial ammonia was introduced into the reaction tube directly from a steel bomb through a flow-meter The nickel rod was replaced by a steel one The receiver was removed as unnecessary The apparatus shown in Fig 1 was also used for the preparation of molybdenum and tungsten dioxydichlorides

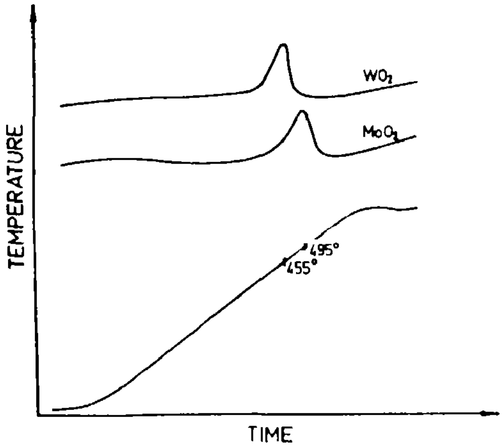


Fig 2

The analyses of reaction products which were carried out by ignition in a stream of oxygen at 550°C showed only a slight difference (0 03 per cent max) from the theoretical content of molybdenum and tungsten in MoO_2 and WO_2

In order to determine the temperature of oxidation of molybdenum (IV) and tungsten (IV) oxides, differential thermal analysis was used (Fig 2) It is evident that oxidation proceeds in a single phase, contrary to uranium (IV) oxide, showing distinct maxima at the temperatures of oxidation

Molybdenum and tungsten dioxydichlorides

In order to prepare pure molybdenum dioxydichloride, free from other reaction products, the chlorination of molybdenum (VI) oxide was carried out with carbon tetrachloride vapour in an oxygen atmosphere using oxygen of commercial purity The oxygen, at a high flow-rate (about 280 ml/min) bubbled through a heated flask containing carbon tetrachloride and then passed through the apparatus shown in Fig 1 The most rapid reaction was found using slightly pressed pellets of molybdenum (VI) oxide placed in a Gooch crucible The receiver was heated with a heating tape in order to prevent the condensation of the products of pyrolysis of carbon tetrachloride

Since the oxidation of the different tungsten chlorides and oxychlorides, occurring as impurities in the tungsten dioxydichloride preparation, proceeds only to the tungsten oxytetrachloride, it was evident that the method used in the molybdenum dioxydichloride preparation could not be used The oxidation of tungsten oxytetrachloride is slow and incomplete, but its sensitivity to moisture (hydrolysis) like all molybdenum and tungsten compounds having a high chlorine content, is much greater than that of tungsten dioxydichloride Therefore the chlorination of tungsten (VI) oxide was carried out in the presence of water vapour at a partial pressure of about 42 mm of mercury In this way, partial hydrolysis of the tungsten oxytetrachloride took place, with formation of tungsten dioxydichloride

The products obtained are very pure, molybdenum dioxydichloride formed large pale to golden-yellow leaflets, and tungsten a lemon yellow crystalline powder After careful drying in high vacuum we kept the samples in sealed ampoules unchanged for a long time

EXPERIMENTAL

Molybdenum (IV) oxide Molybdenum (VI) oxide (15 g) was placed in a Gooch crucible which was introduced into a vertical furnace as shown in Fig 1 The flow-rate of ammonia was 60 ml/min Reduction was carried out at a temperature of 460 C during 25 min The temperature was regulated by means of a variable transformer and measured with nickel-nichrome thermocouple Molybdenum (IV) oxide in the form of a brown powder, was left overnight over concentrated sulphuric acid Analysis, ignition at 550 C to molybdenum (VI) oxide gave Mo 75 00, MoO_2 requires Mo, 74 99%

Tungsten (IV) oxide Tungsten (VI) oxide (15 g) was placed in a Gooch crucible which was put in the reaction tube as described for molybdenum (IV) oxide The flow-rate of ammonia was about 60 ml/min The reaction temperature of 580 C was kept constant during 90 min Tungsten (IV) oxide, in the form of a brown powder was left overnight over sulphuric acid Analysis, ignition at 550 C to tungsten (VI) oxide gave W, 85 14 WO_2 requires W, 85 17%

Molybdenum dioxydichloride Molybdenum (VI) oxide pellets (3 10 mm dia 15 g) were placed in a Gooch crucible which was then put in the reaction tube represented in Fig 1 Chlorination was carried out at a temperature of 550 C during 45 min The oxygen flow-rate was about 260 ml/min The temperature of the carbon tetrachloride was 25°C Molybdenum dioxydichloride was accumulated in the receiver as large yellow leaflets Yield quantitative Analysis, precipitation of the molybdenum as $PbMoO_4$(14) gave Mo, 48 23, MoO_2Cl_2 requires 48 45%

Tungsten dioxydichloride Tungsten (VI) oxide pellets (3 × 10 mm dia 9 g) were placed in the reaction tube as described above The chlorination was carried out at the temperature of 370°C during 1 hr The oxygen flow-rate was about 280 ml/min, the temperature of the carbon tetrachloride, with the water layer over it, was 35°C Tungsten dioxydichloride in the form of small lemon yellow crystals was dried in high vacuum over phosphorus pentoxide Yield quantitative Analysis, by precipitation of tungsten with 8-hydroxyquinoline (15) Tungsten weighed as $WO_2(C_9H_6ON)_2$ gave W, 64 12, WO_2Cl_2 requires W, 64 36%

Acknowledgement—Thanks are due to Professor D GRDENIC for his interest during our work

(14) *Scott's Standard Methods of Chemical Analysis* (5th Ed) p 598 Van Nostrand, New York (1954)

(15) A VOGEL, *A Textbook of Quantitative Inorganic Analysis* (2nd Ed) p 492 Longmans, London (1951)

J. Inorg. Nucl. Chem. 1963, Vol. 25, pp. 1119 to 1127. Pergamon Press Ltd. Printed in Northern Ireland

THERMAL DECOMPOSITION OF YTTRIUM OXALATE IN VACUUM AND IN VARIOUS ATMOSPHERES*

A. GLASNER, E. LEVY and M. STEINBERG
Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Israel

(*Received* 7 *January* 1963)

Abstract—Yttrium oxalate may be dehydrated in vacuum at a temperature as low as 260°, and decomposition of the oxalate itself begins upon completion of dehydration. In vacuum as well as in an open furnace, various carbonato-oxalates and oxycarbonates are formed in the temperature range 300–420°. Disproportionation of the carbon monoxide originating from the initial decomposition of the oxalate takes place to an extent of nearly 60 per cent. The carbon thus deposited stabilizes the oxycarbonate, CO and CO_2 being evolved only on heating at 700–1000°. In an oxidizing atmosphere the carbon is burned away, and white Y_2O_3 may be obtained at 420° under proper conditions.

THERE has recently been wide interest in the thermal decomposition of rare earth oxalates and in the oxalates of some related metals. The thermal decomposition of yttrium oxalate, for one, has been investigated by several authors using the thermogravimetric[1–3] and the differential thermal analysis[2,4] methods. Results obtained by some authors indicate that a higher hydrate is converted below 200° to the dihydrate. The latter is considered stable up to 260°, and thereupon slowly loses water up to about 410°, when the anhydrous oxalate is obtained and soon starts decomposing, to yield, in one continuous step, the oxide at about 640°. On heating a sample for 30 min at 468°, an oxycarbonate was isolated,[2] which was proved by analysis to have the composition $(YO)_2CO_3$.

The DTA curves[2,4] show an exothermic peak just above 600°, which is attributed[4] to the formation of a new oxide phase (amorphous → crystalline). Such exothermic peaks were noted by WENDLANDT *et al.*[5] mostly in the temperature range 600–700°C on all of the DTA curves of rare earth oxalates studied by them. They suggest that these exothermic peaks are due to an oxidation process, but are unable to offer any explanation for their presence.

In our studies of the thermal decomposition of rare earth oxalates in vacuum[6–8] it was shown that a disproportionation of carbon monoxide primarily released takes place, causing a darkening of the residue by the carbon left over. Hence it seems plausible that the exothermic peaks observed with yttrium and other rare earth oxalates are due to the burning of this previously deposited carbon under conditions where access of air is limited.

---

* This article is part of a Ph.D. thesis submitted by E. L. to the Senate of the Hebrew University of Jerusalem.

[1] W. W. WENDLANDT, *Analyt. Chem.* **30**, 58 (1958).

[2] R. P. AGARWALA and M. C. NAIK, *Analyt. Chim. Acta* **24**, 128 (1961).

[3] YA. S. SAVITSKAYA, M. A. GUREVICH, S. V. KALABUKHOVA and S. I. SITNIKOVA, *Russ. J. Inorg. Chem.* **5**, 1114 (1960), *Zh. Neorg. Khim.* **5**, 2300 (1960); YA. S. SAVITSKAYA, N. N. TVOROGOV, C. V. KALABUKHOVA and L. S. BRYKINA, *Ibid.* **7**, 2029 (1962).

[4] S. L. BLUM and E. A. MAGUIRE, *Amer. Cer. Soc. Bull.* **39**, 310 (1960).

[5] W. W. WENDLANT, T. D. GEORGE and G. R. HORTON, *J. Inorg. Nucl. Chem.* **17**, 273 (1961).

[6] A. GLASNER and M. STEINBERG, *J. Inorg. Nucl. Chem.* **16**, 279 (1961).

[7] A. GLASNER and M. STEINBERG, *J. Inorg. Nucl. Chem.* **22**, 39 (1961).

[8] A. GLASNER and M. STEINBERG, *J. Inorg. Nucl. Chem.* **22**, 156 (1961).

The aim of the present work was to obtain more detailed information on the thermal decomposition of yttrium oxalate and the possible existence of intermediate products.

EXPERIMENTAL

Materials. The yttrium oxalate used in this work was prepared from the oxide (Lindsay Co., Code no. 1116 99.9 per cent purity) by dissolution in dilute nitric acid and precipitation by the addition of successive portions of a 1 M-$H_2C_2O_4$ solution. After standing overnight on a water bath at 60°, the crystals were filtered, dried and kept in a desiccator over P_2O_5.

The yttrium oxide content of the crystal hydrates was determined by ignition to 1000°C, and that of the oxalate by titration with permanganate, proving that their composition was $Y_2Ox_3 \cdot 3.6H_2O$.

Dehydration was effected by heating the crystals in vacuum for 30 min at 260°. After this treatment, the oxalate was still found to contain 0.2 per cent water, but more prolonged heating, even at a somewhat lower temperature, caused an initial decomposition of the oxalate itself.

Experiments in vacuum were carried out with dehydrated samples, whilst for decompositions under various atmospheres the hydrated salt was used.

Apparatus and techniques. The vacuum apparatus used was described earlier.(6) In a few experiments in which the samples were heated up to 1000°, the Pyrex reaction tube was exchanged for a silica tube. At the end of each run, the accumulated partial pressures of CO and CO_2 were determined, and the infra-red absorption spectra of most of the solid residues were examined by the KBr disk method.

For experiments for decompositions in various atmospheres (air, O_2, N_2, CO_2) an open tube oven was used, through which a continuous current of gas, previously dried over anhydrone (84 ml/min), was allowed to flow. The oven was brought to the desired constant temperature, and then a sample of yttrium oxalate hydrate weighing 50–170 mg was introduced in a porcelain boat. After heating for 24 hr at least, the loss of weight and carbonate content of the residues were determined. A weighed portion of the residue was allowed to react with mineral acid (H_3PO_4) and the CO_2 released was driven over by a current of pure nitrogen and absorbed in ascarite tubes. The infra-red spectrum of most of the residues was also recorded.

RESULTS

1. *Dehydrated samples heated to* 1000° *in vacuum*

Results of gasometric measurements in this series of experiments are recorded in Table 1, showing the partial pressures of CO and CO_2 obtained on heating for 24 hr. Samples of Y_2Ox_3 weighing 9.33 mg were used in all these experiments (excepting *B*, which weighed 7.15 mg, in the latter case the actual pressures measured are also given in brackets). The expected total pressure on decomposition according to the equation

$$Y_2(C_2O_4)_3 \rightarrow Y_2O_3 + 3CO + 3CO_2$$

was 484 μ. The measured total pressures were always lower, the difference being 31 μ on the average for A and B, and 60 μ for C and D. Also, the partial pressure of CO was always less, and that of CO_2 always more than expected (242 μ). The excess of CO_2 pressure was 30 μ—average for the four experiments—indicating that a corresponding amount of CO (about 25 per cent) underwent disproportionation $2CO \rightarrow CO_2 + C$. The residues were coloured black by the carbon deposited, and the infra-red absorption spectra were blank in the 5 μ–15 μ region, with the exception of a small residual absorption at 6.2 μ (see Fig. 2). This proves that the oxalate completely decomposes to Y_2O_3, but the deposited carbon may be chemically combined.

In experiments C and D (Table 1) the samples were intermittently heated for 24 hr at the indicated temperatures. At each step the reaction vessel was isolated from the body of the gasometer by shutting the stopcock, the partial pressures were determined and the gases pumped off, before raising the temperature to the next step.

TABLE 1. PARTIAL PRESSURES OF CO AND CO_2 EVOLVED ON HEATING Y_2Ox_3 UP TO 1000 IN VACUUM. WT OF SAMPLES 9.33 mg, TOTAL PRESSURE EXPECTED 484 μ

	Temp (°C)	Observed pressure (μ) CO	CO_2	Total
A	1000	180	270	450
B	1000	176	280	456
		(135)	(215)	(350)
C	400	115	155	270
	500	3	33	36
	600	0	43	43
	700	3.5	15.5	19
	800	7	16	23
	1000	26	4	30
		154.5	266.5	421
D	750	130	270	400
	1000	25	2	27
		155	272	427

It is seen that the greater part of the CO is evolved at 400° and that at temperatures above 700° the evolving gases again contain CO in proportions increasing with temperature. Hence it may be concluded that Y_2Ox_3 decomposes at 400° leaving a residue of oxycarbonate admixed with carbon, and at higher temperatures the two solids react, to give a mixture of CO and CO_2.

The estimated disproportionation of CO, originating from the oxalate in experiments C and D, is thus found to be about 50 per cent.

2. *Decomposition in vacuum*

Samples weighing 6.9 mg Y_2Ox_3 were heated in vacuum at constant temperatures from 300 to 420°C. A plot of pressure vs time curves standardized for 6 mg samples is shown in Fig. 1. At 300 the decomposition is rather slow and apparently did not finally steady down even after 45 hr heating. At 390 and 420° on the other hand the main reaction seems to have been completed in less than 30 min followed by a slow continued evolution of gases for 24 hr. There is also a break in the curves after the accumulation of about 10 per cent of the final pressure, most evident in the 360 run. Because of all these complications no simple rate equation could be suited to the reaction curves. A rough estimation of the activation energy is 37 kcal/mole.

The actual weights of the samples, the expected pressures on decomposition to the oxide and the final partial pressures of CO and CO_2 obtained at the temperatures shown are recorded in Table 2. All residues were brown, having a lighter tint at the lower temperatures. The CO_2 partial pressures always exceeded the CO, the ratio $\mu CO_2/\mu CO$ rising with temperature from 1.34 at 300° to 1.48 at 420°. Also, the combined partial pressures were somewhat less than half the expected pressure and matched the latter only at the higher temperatures.

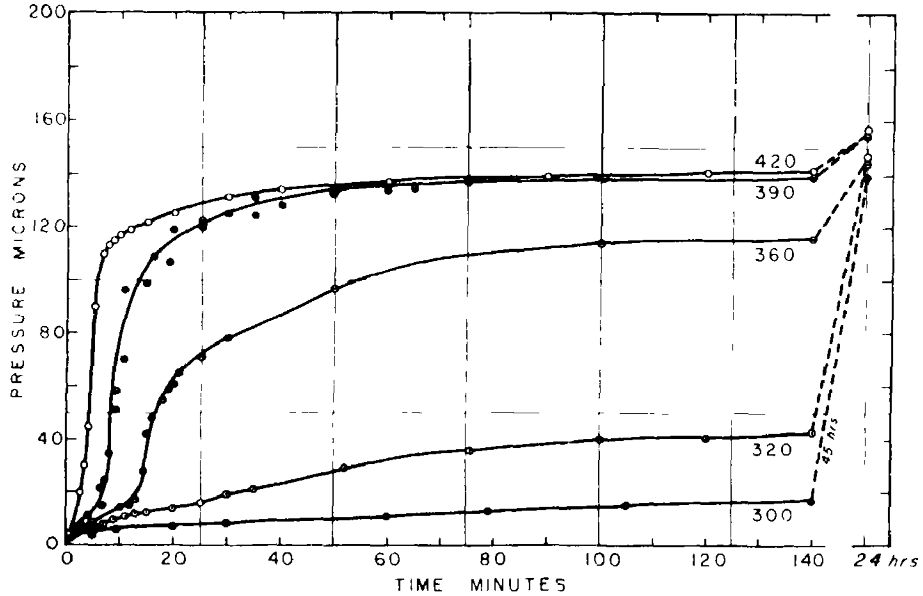


FIG. 1.—Decomposition vs. time curves of Y_2Ox_3 in vacuum.

TABLE 2.—PARTIAL PRESSURES OF CO AND CO_2 EVOLVED ON HEATING Y_2Ox_3 FOR 24 HR IN THE TEMPERATURE RANGE 300–420°

Temp (°C)	Wt of sample (mg)	Expected total pressure	Partial pressure (μ) CO	Partial pressure (μ) CO_2
300*	5.97	310	59	79
320	6.61	343	69	93
360	7.91	411	83	110
390	6.00	312	64	91
390	6.84	355	75	105
420	9.01	468	94	139

* heated for 45 hr

The infra-red spectra show (Fig. 2) that the solid residues contained only carbonate, but no oxalate, with the exception of the residue heated at 300° for 45 hr, where absorption bands characteristic for oxalate ion are also present.

Hence it may be concluded that at any temperature above 320°, Y_2Ox_3 completely

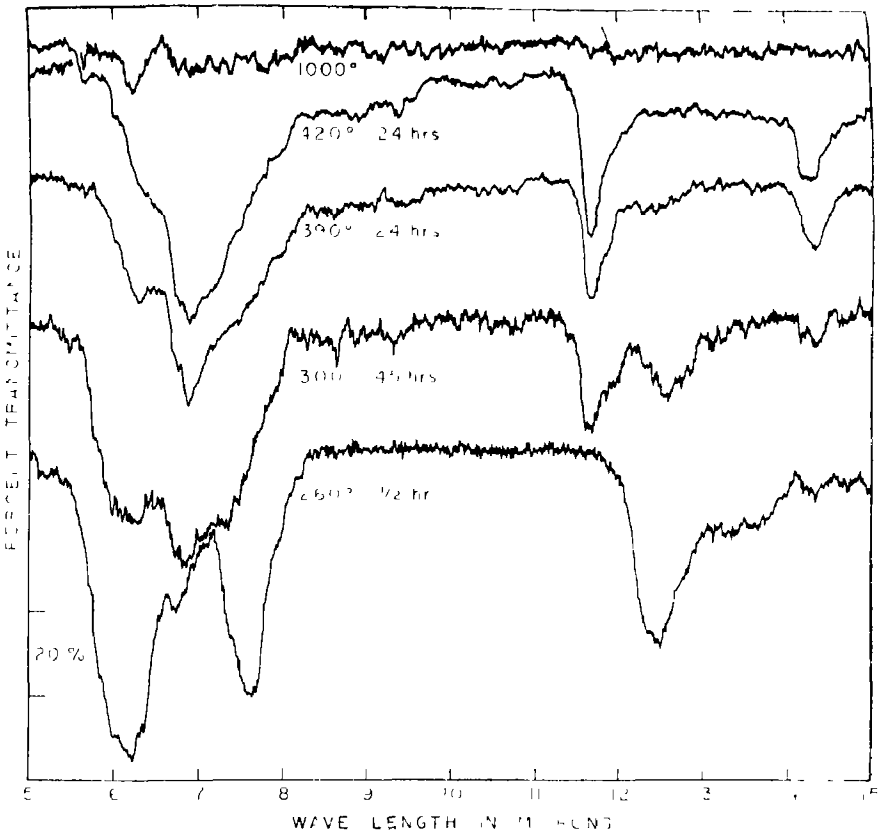


FIG 2 Infra-red absorption spectra of residues obtained on heating Y_2Ox_3 in vacuum for the time and at the temperatures indicated

decomposes into the carbonate, and the low partial pressure of CO is due to an extensive disproportionation of this gas

In Table 3, the partial pressures of CO and CO_2 were converted into percentages

TABLE 3 PER CENT OF GASES EVOLVED, AND ESTIMATED COMPOSITION OF RESIDUES

Temp (C)	CO (%)	CO_2 (%)	CO_2 (%) (from carbonate)	Approximate composition of residue	
300	38 1	51 0	23 4	$Y_2Ox_{0\ 5}(CO_3)_{2\ 25}$	$C_{0\ 9}$
320	40 2	54 2	24 6	$Y_2Ox_{0\ 5}(CO_3)_{2\ 25}$	
360	40 4	53 5	23 9	$Y_2Ox_{0\ 5}(CO_3)_{2\ 25}$	
390	41 0	58 3	28 7	$(YCO_3)_2O$	
390	42 3	59 1	29 5	$(YCO_3)_2O$	
420	40 2	59 4	29 8	$(YCO_3)_2O$	
Mean	40 8				

of the expected pressures, revealing that only 40 8 % of the expected CO has evolved, this value being constant in the whole range of temperatures at which measurements were made Therefore 59 2 per cent of the CO underwent disproportionation, accounting for 29.6 per cent of the CO_2, while the remainder (listed in column 4 Table 3) must have come from further decomposition to oxycarbonates (column 5). After allowing for 6.75 per cent of undecomposed oxalate at 300°, the oxycarbonate $Y_2O_{0.7}(CO_3)_{2.3}$ is evidently stable in the temperature range 300–360° and the oxycarbonate $(Y_2CO_3)_2O$ in the range 390–420° admixed in both cases with $C_{0.9}$ carbon.

3. *Decomposition of Y_2Ox_3 hydrate under atmospheric pressure of various gases*

Experiments were carried out at four different temperatures in the range 320–420°. The results are summarized in Table 4, showing the per cent loss of weight after heating for 24 hr in the atmosphere and temperature indicated— and the weight per cent of CO_2 in the residue. Comparing these two data to the corresponding values calculated for all possible decomposition products, listed in Table 5, the composition of the residues may be determined, as shown in the last column of Table 4. The

TABLE 4. LOSS OF WEIGHT AND PERCENTAGE OF CO_2 IN SOLID RESIDUE, FORMED ON HEATING Y_2Ox_3 3.6H_2O IN VARIOUS ATMOSPHERES

Temp (°C)	Atmosphere	Wt of sample	Loss of wt (%)	CO_2 in residue (%)	Colour of residue	Composition of residue
320	Air	110.8	23.6	21.0	White	$(YCO_3)_2C_2O_4$
320	Oxygen	122.3	24.0	20.7	White	$(YCO_3)_2C_2O_4$
320	Nitrogen	177.3	23.7	20.5	Brown	$(YCO_3)_2C_2O_4$
320	CO_2	151.2	17.9	10.2	Brown	$(YC_2O_4)_2CO_3$
360	Air	49.4	39.6		White	$(YCO_3)_2O$
360	Oxygen	87.7	39.5	27.9	White	$(YCO_3)_2O$
360	Nitrogen	89.8	39.9	27.3	Beige	$(YCO_3)_2O$
360	CO_2	88.6	23.5	22.0	Beige to brown	$(YCO_3)_2C_2O_4$
390	Air	120.3	46.5	16.2	White	$(YO)_2CO_3$
390	Oxygen	118.9	46.4	—	White	$(YO)_2CO_3$
390	Nitrogen	124.0	46.5	16.0	Brown	$(YO)_2CO_3$
390	CO_2	129.2	39.9	27.4	Brown	$(YCO_3)_2O$
420	Air	119.3	55.3	—	White	Y_2O_3
420	Oxygen	113.2	55.2	0	White	Y_2O_3
420	Nitrogen	116.1	55.3	0	Light brown	Y_2O_3
420	CO_2	119.3	47.0	16.0	Grey-brown	$(YO)_2CO_3$

TABLE 5. THEORETICAL LOSS OF WEIGHT OF Y_2Ox_3 3.6H_2O, AND PER CENT OF CO_2 IN POSSIBLE DECOMPOSITION PRODUCTS

Composition	Loss of weight (%)	CO_2 in residue (%)
Y_2Ox_3	12.80	0
$(YOx)_2CO_3$	18.33	10.63
$(YCO_3)_2Ox$	23.86	22.80
$Y_2(CO_3)_3$	29.38	36.87
$(YCO_3)_2O$	38.06	28.06
$(YO)_2CO_3$	46.75	16.31
Y_2O_3	55.43	0

correspondence in all cases is close enough for both values compared to make the identification plausible The composition of the residues has also been qualitatively confirmed by infra-red spectra (see Fig 3)

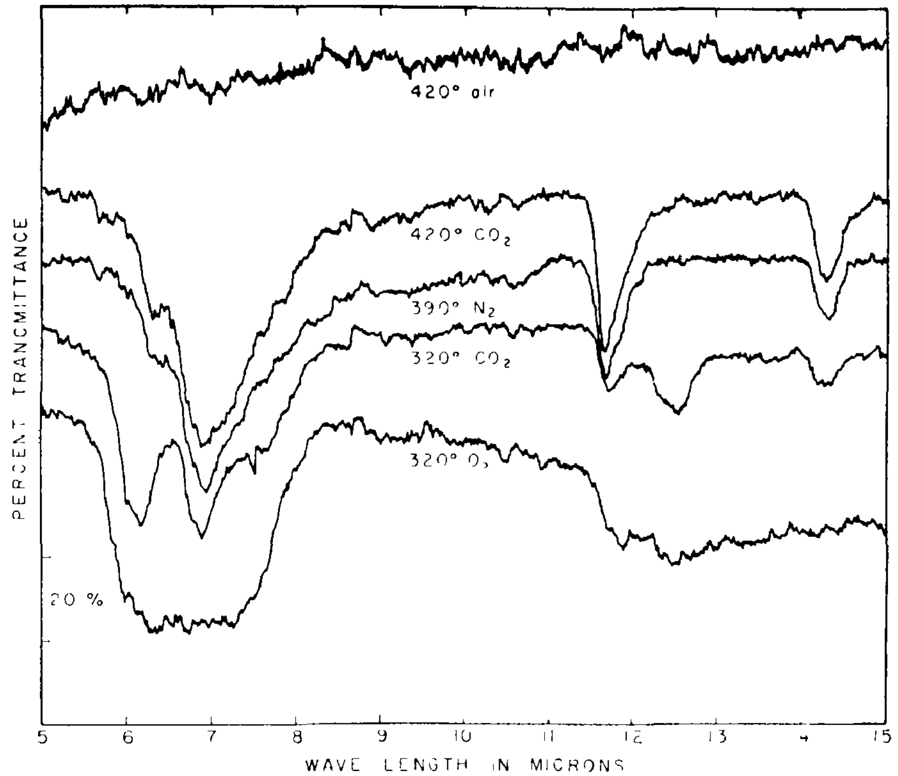


FIG. 3—Infra-red absorption spectra of residues obtained on heating Y_2Ox_3 3 6H_2O for 24 hr at the temperatures and atmospheres indicated

The residues from decomposition in nitrogen or CO_2 were beige to brown, while in air or oxygen they were white, i e the carbon burned away in the latter atmospheres and was not deposited

The compositions of the residues obtained in nitrogen were identical with those of the residues obtained in air or oxygen, at all temperatures, a stable carbonato-oxalate is formed in these atmospheres at 320°, but at 420 there is complete decomposition to the oxide Y_2O_3 On comparing these results with those obtained in vacuum, it may be noted that atmospheric pressure retards the decomposition of the oxalate, but furthers the decomposition of the carbonate at 390° as well as at 420

The stabilization effect of the CO_2 atmosphere on the oxalates is even more pronounced, but even in this atmosphere the carbonate content of the residue $(YO)_2\,CO_3$ obtained at 420° is lower than that formed in vacuum $(YCO_3)_2O$

DISCUSSION

It has been proved in this work that $Y_2Ox_3\,nH_2O$ can be completely dehydrated in vacuum at temperatures below 260° Decomposition of the oxalate itself begins soon after dehydration and the rate can be comfortably measured at 300°, although it is rather slow at this temperature. The much higher temperature of decomposition (415°) indicated by thermogravimetric and DTA measurements[1,2] can be attributed to the very slow rate of dehydration under atmospheric pressure in partly closed vessels.

In the temperature range 300–420° various carbonato-oxalates and oxy-carbonates are formed in different atmospheres as well as in vacuum. The carbonate $Y_2(CO_3)_3$ itself was not obtained under any condition, giving the impression that yttrium carbonate is less stable than the oxalate. In an oxidizing or inert atmosphere (nitrogen) with continuous flow of gases, decomposition to the oxide Y_2O_3 is already completed at 420°. In vacuum, on the other hand, an oxycarbonate $(YCO_3)_2O$, with a relatively high carbonate content, is stabilized at this temperature.

Some of the gases retained in the partly decomposed residues may be driven out only on heating for long periods at 700–1000°. For example, in experiment C (Table 1), 17 per cent of the total amount of gases were evolved in this range of temperatures. The phenomenon may be connected with the disproportionation of the carbon monoxide, on prolonged heating at the lower temperatures, the deposited carbon combines with the carbonate, probably giving anions[9,10] of the type $C_nO_n{}^{m-}$, which decompose only on being heated to temperatures above 700°.

In vacuum, 59.2 per cent of the CO expected to evolve from Y_2Ox_3 undergoes disproportionation, depositing 0.444 atoms of carbon per ion of yttrium. For comparison, it has been shown[8] that 70 per cent of the CO from Ce_2Ox_3 disproportionates, and therefore 0.525 atoms of carbon per ion of cerium should be deposited on decomposition at 340–420° in vacuum. It is interesting to note that other workers[11] obtained, at 350°, under similar conditions, a residue of cerous carbonate which contained very nearly the same surplus of carbon: $Ce_2C_{4.1}O_{9.1}$. On heating this compound for 24 hr at 600°, it tenaciously retained, even at this temperature, an oxycarbon compound together with the surplus carbon: $Ce_2C_{1.25}O_{3.99}$.

In a stream of air or oxygen no carbon is deposited, but it is oxidized to CO_2 as evidenced by the white colour of the residues. This explains the early decomposition of the intermediate carbonate and the formation of the oxide Y_2O_3 at the comparatively low temperature of 420°. On the other hand, the identity of the composition of the brown residues obtained in a nitrogen atmosphere with those of the white residues formed in the oxidizing atmospheres is rather puzzling. The reason for this anomalous behaviour should be sought in the experimental conditions; the hydrated samples used in these experiments were dehydrated at a much faster rate by the current of dry gases than under usual conditions of heating in a closed, or partly closed, vessel. Apparently the anhydrous solid oxalate thus obtained is very reactive owing to its metastable open structure, and releases CO and CO_2 at a faster rate than the more compact anhydrous solid. This surmise has been partially confirmed by heating hydrated samples in vacuum, when faster decomposition rates were actually observed. On the other hand, dehydrated samples heated in a stream of nitrogen at 420° lost only 42.3–42.4 per cent of their weight. Calculated on the basis of the hydrate $Y_2Ox_3\ 3.6H_2O$ this is equivalent to a loss of 49.73 per cent instead of 55.3

(9) R. WEST, H. Y. NIU, D. L. POWELL and M. V. EVANS, *J. Amer. Chem. Soc.* **82**, 6204 (1960).

(10) R. WEST and HSIEN YING NIU, *J. Amer. Chem. Soc.* **84**, 1324 (1962).

(11) O. K. SRIVASTAVA and A. R. VASUDEVA MURTHY, *J. Sci. Industr. Res.* **20 B**, 96 (1961).

per cent recorded in Table 4. The CO_2 released on treating the greyish-brown residue with acid was only 5 2–5 3 per cent, as compared to ~11 0 per cent expected (see Table 5) Evidently, the deposited carbon renders the residual carbonate less reactive and complicates its determination by the usual methods (6)

Conditions in TG and DTA measurements seemingly resemble those in the present work in vacuum, dehydration being slow and access of oxygen (air) limited Hence, following disproportionation the carbonate is stabilized and the carbon is burned away only in the neighbourhood of 600°, about the same temperature as the exothermic peaks observed(5) with other rare earth oxalates

Unless the cation is reducible (like europium) or oxidizable (like cerium), the various phenomena and sequence of reactions discussed here in the case of yttrium oxalate are repeated with the rare earth and with other oxalates There are two factors differentiating between these oxalates with respect to the various stable intermediates formed

(a) Small cations with a high charge tend to form very stable hydrates, and their thermal dehydration is always attended with decomposition of the oxalate Hence, the normal oxalates cannot be prepared by this method

(b) In a series of equicharged cations (for example, the tervalent rare earths) the oxalates are more stable the smaller the radius of the cation (7) No similar stabilizing effect occurs with the carbonate ion,(8) and therefore no intermediate normal carbonates of the yttrium group are ever formed on the thermal decomposition of their oxalates

J. Inorg. Nucl. Chem. 1963, Vol. 25, pp. 1129 to 1132. Pergamon Press Ltd. Printed in Northern Ireland

THE THERMAL DECOMPOSITION OF LEAD NITRATE*

F. Vratny† and F. Gugliotta‡
Purdue University, Chemistry Department
West Lafayette, Indiana

(*Received* 17 *December* 1962, *in revised form* 4 *March* 1963)

Abstract—The thermal decomposition of lead nitrate has been investigated in the temperature range from 250 to 435°C. Information obtained from the infra-red analysis of the decomposition products indicate that the reaction proceeds via a basic nitrate or metallic nitrite structure, while gasometric analysis indicates that the decomposition proceeds essentially via the loss of nitrogen oxide and oxygen, without significant oxidation of the lead ion.

The thermal decomposition of lead nitrate has been investigated as part of a programme to investigate the interaction of nitrogen dioxide and metallic oxides. It has been found in preceding investigations,[1,2] that nitrogen dioxide is the prime decomposition product in the decomposition of nitrates. Further, the effect of the decomposition is such that oxidation of the metallic ion can be initiated. In particular, in the decomposition of cerium [III] nitrate[2] the decomposition leads directly to cerium dioxide under all conditions, with an apparent progression in oxidation states as the decomposition proceeds. In the case of the decomposition of praseodymium nitrate the picture is considerably complicated by a whole progression of oxidation states from an effective oxidation state of Pr(III) to Pr(IV). The picture is further complicated by the appearance of intermediate nitrate-nitrite products.

The present investigation has been conducted as an extension of the above work with consideration given to the variable oxidation state of lead as well as the greater instability of the higher oxides of lead.[3] As in the preceding work gasometric and infra-red analysis of the decomposition products was used as a means of following the reaction path.

RESULTS

The material used in this study was a single batch of high purity Baker lead nitrate. This material was desiccated under vacuum over magnesium perchlorate and weighed in desiccated containers. The samples were then placed in the decomposition chamber,[1] which consisted of an oil manometer and associated traps. The sample was then raised to the desired temperature within a period of 1–3 min. The reaction was followed by means of the oil manometer as previously described. The pressure–time curve was found to assume a sigmoidal shape as indicated in Fig. 1.

---

* This work was carried on at Purdue University under a grant from The Lincoln Laboratories of the Mass. Inst. of Tech. which is an organization under the joint support of the United States Army, Navy and Air Force.

† Presently at Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey.

‡ Presently at National Cash Register, Cleveland, Ohio.

(1) F. Vratny and J. M. Honig, *Trans. Faraday Soc.* 451 **56**, 1051 (1960).

(2) F. Vratny, S. Kern and F. Gugliotta, *J. Inorg. Nucl. Chem.* **17**, 281 (1961).

(3) J. S. Anderson and M. Sterns, *J. Inorg. Nucl. Chem.* **11**, 272 (1959).

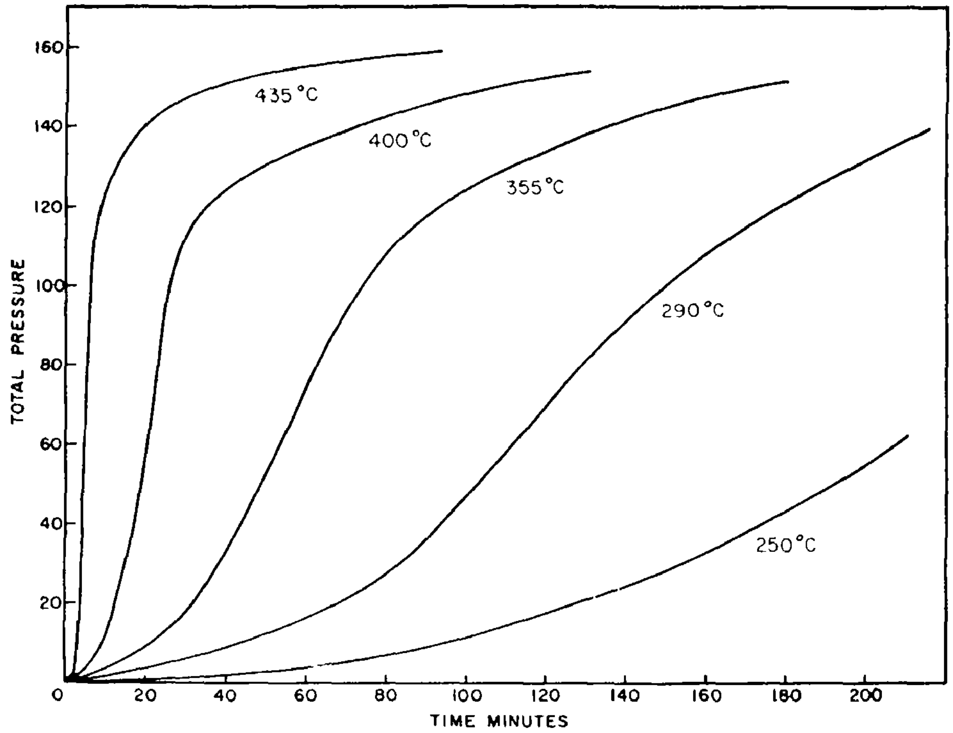


FIG. 1 Kinetics of the thermal decomposition of lead nitrate, total pressure in mm vs time in min

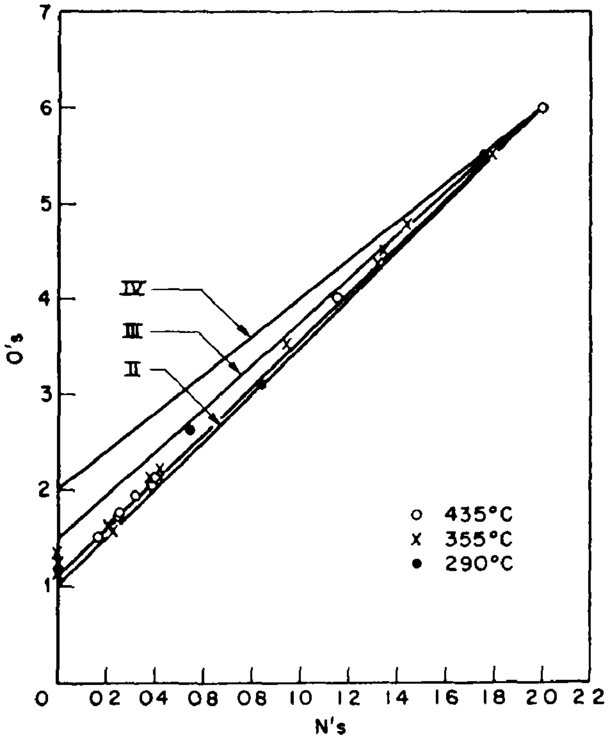


FIG 2 – Composition correlation in the thermal decomposition of lead nitrate, oxygen stoichiometry vs nitrogen stoichiometry, II, III, IV indicates the theoretical oxidation axis for the lead ion

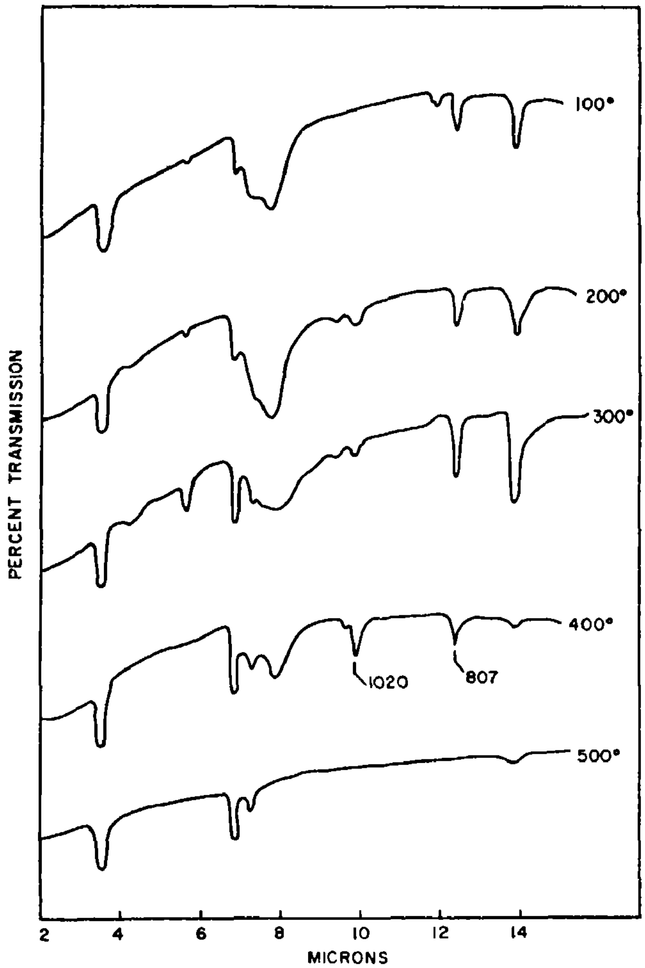


FIG 3—Infra-red spectra of the decomposition products of lead nitrate obtained at various temperatures, spectra obtained in Nujol with rock salt optics

It may be seen in this figure that at the lowest temperature (250 C) the decomposition is approximately 30 per cent complete in 200 min while at 400°C the reaction is essentially complete in 50 min

Gas analysis was performed by condensation of the nitrogen dioxide at liquid nitrogen temperatures to obtain the partial pressure of oxygen Upon removal of the oxygen the partial pressure of NO_2-N_2O_4 was obtained The absence of the lower oxides of nitrogen was established by the absence of a discoloration of the condensate and by the infra-red analysis of the gas Details of the analysis are given in Reference (1)

It was found from the above analysis that the oxygen nitrogen content of the decomposition products executed a straight line through the composition $Pb(NO_3)_2$ and PbO as seen in Fig 2 Thus, one may presume that the oxidation state of the lead ion remained essentially divalent (II) as indicated by the correlation with the theoretical divalent axis The fact that some oxidation has occurred is borne out by the scatter of points between the (II) and (III) oxidation co-ordinates

On conclusion of the decomposition run, the sample was subjected to infra-red analysis The spectrum was obtained in the 2 to 15 μ region in a Nujol null A representative progression is shown in Fig 3 for products obtained at increasing decomposition temperatures Nujol lines are evident at ~3 5, 6 8 and 7 3 μ The bands at ~7 4, 7 6 7 8, 12 4 and 13 9 μ are due to the presence of metallic nitrate (4) It may be seen that as the decomposition temperature is increased the intensity of these bands decrease Further in evidence are two bands at ~9 3 and 9 8 μ These bands are due to the presence of metallic nitrite(5) and as such occur at intermediate stages of the decomposition

DISCUSSION

In contrast to the decomposition of cerium (III) nitrate the present study indicates that the lower oxidation state is preferred under the conditions of the decomposition The scatter of points above the (II) oxidation axis and below the (III) axis is strongly in accord with the work of Anderson and Sterns(3) who found that the monoxide of lead can be oxidized under modest conditions to the nonstoichiometric intermediate of PbO_x where 1 0 x 1 5 In general this transition was found to be strongly time dependent requiring as much as 20 hr at 310°C and 600 mm P_{O_2} to reach $PbO_{1 5}$ It is therefore not surprising that the presence of a partial pressure of 60 to 100 mm of oxygen and/or nitrogen oxide has no greater effect than that noted in Fig 2 It is suggestive in this regard that the egress of nitrogen oxide and oxygen from lead nitrate leave the lead as Pb(II) and only on extended exposure does the transition-up in oxidation state occur A further point in evidence of the direct egress of NO_2 is indicated by the nitrite structure which occurs in the intermediate decomposition regions and can conceivably act as a decomposition intermediate to nitrogen dioxide The next logical step in this study is an investigation of the interaction of lead monoxide and nitrogen dioxide (6)

(4) F Vratny, *Appl Spect* **13**, 59 (1959)

(5) F Vratny, M Tsai, F Gugliotta *Nature (Lond)* **188**, 4749, 484 (1960)

(6) F Vratny, J M Honig, *Trans Faraday Soc* 463, **57**, 1176 (1961)

J. Inorg. Nucl. Chem. 1963 Vol. 25 pp. 1133 to 1137. Pergamon Press Ltd. Printed in Northern Ireland

HIGH PRESSURE REACTIONS OF CaO AND CdO WITH URANIUM OXIDE*

A. P. YOUNG and C. M. SCHWARTZ
Battelle Memorial Institute, Columbus, Ohio

(*Received* 3 *January* 1963, *in revised form* 4 *March* 1963)

Abstract—Mixtures of uranium oxide and bivalent metal oxides were reacted at 60,000 atm pressure and 900–1200°C temperature.

CaU_3O_{8+x} compounds with Cu_3Au-type ordering of uranium and calcium ions were synthesized at high pressure. This is probably the first instance of Cu_3Au-type cation ordering in a mixed oxide. Ordering was dependent on oxygen content. High pressure compounds with compositions CaU_3O_9 and $CaU_3O_{8.8}$ were ordered. High pressure compounds with compositions $CaU_3O_{8.6}$, $CaU_3O_{8.4}$ and $CaU_3O_{7.75}$ were face-centred cubic. The dependence of ordering on oxygen content can be explained qualitatively if oxygen is assumed to go into cell centres in a CaU_3O_{8+x} fluorite-type structure. No superlattice reflections indicative of ordering of U and Cd ions were observed in high pressure CdU_3O_8.

High pressure $CaUO_3$ was face-centred cubic.

THE work of WILSON[1] on the effect of pressure on the uranium-oxygen system disclosed a new polymorph of U_3O_8, occurring at pressures above 16,000 atm and temperatures above 400°C. Also, a cubic modification of U_3O_8 was found at pressures above 70,000 atm. The determination by WILSON of the effects of ultrahigh pressure on uranium oxides was undertaken as a prerequisite to the study of the effects of pressure on reactions of uranium oxide with other oxides.

In the present work, uranium oxide was reacted with CaO and CdO at 60,000 atm pressure and at temperatures from 900°–1200°C. For comparison with high pressure results, some mixtures were reacted at the same temperatures at ambient pressure in air or in an inert atmosphere.

EXPERIMENTAL PROCEDURE

For the investigation of the effects of combined pressure and temperature on mixed oxide reactions, a version of the "Belt" apparatus described by Hall was used. Sample pressures to 60,000 atm were obtained routinely in this apparatus without excessive piston or die breakage. The pressure scale was based on the calibration scheme suggested by KENNEDY[2] in which the Ba(II)–Ba(III) transition occurs at 60,000 atm.

A typical mixed oxide sample was prepared by weighing the powder constituents in the proper proportions and grinding in a tungsten carbide mortar. The sample was compacted in a $\frac{1}{16}$ in. o.d. platinum tube with 0.005 in. wall thickness. The tube was closed on both ends with hammered platinum foil. The platinum tube served both as container and heater. The high pressure assembly with pyrophyllite cylinders and gaskets was similar to that described by HALL.[3]

For temperature determination, thermocouples were welded to the platinum capsules. Although the platinum capsule was distorted in the pressure cell, temperature at pressure could generally be

---

* Work performed under AEC Contract W-7405-eng-92.

[1] W. B. WILSON, *J. Inorg. Nucl. Chem.* **1**, 357 (1955).

[2] G. C. KENNEDY and P. N. LAMORI, *Progress in Very High Pressure Research* pp. 304–313. J. Wiley, New York (1961).

[3] H. T. HALL, *Rev. Sci. Instrum.* **31**, 125 (1960).

determined In some samples, hot spots adjacent to thin areas of the heater tube or at a poor end contact were present After a high pressure run, the tube and sample were mounted in epoxy resin and sectioned In some instances, differences in colour in the sample were indicative of temperature gradients in the sample Generally, specimens for X-ray diffraction were taken from the neighbourhood of the thermocouple junction In case of thermocouple failure, sample temperature was estimated from the heater wattage

Because of the small sample size no attempt was made to determine density or oxygen content of high pressure samples There is some evidence from other work that oxygen is generally retained in the high pressure high temperature capsule There was also a systematic change in structure with oxygen content of the initial mixtures in a series of uranium oxide calcium oxide samples described below In the description of results it is assumed that the oxygen content of the high pressure samples was close to that of the initial mixture

The uranium oxide in the initial mixtures was prepared from Mallinkrodt UO_2 Added oxides were Baker Reagent Grade chemicals

RESULTS

High pressure samples with composition CaU_3O_9 were prepared by reacting 1 1 mixtures of CaO and U_3O_8 The X-ray powder pattern of high pressure samples with composition CaU_3O_9 exhibited all the reflexions of a face-centred-cubic structure plus many weaker reflexions indexable on the cubic unit cell The lattice parameter indicated a solid solution of CaO in a UO_{2+x} structure The extra reflexions indicated ordering of some kind

The simplest type of ordering in the samples with strong face-centred-cubic reflexions would be the Cu_3Au type array in the cation lattice with uranium at face centres and calcium at the corners of cube cells Assuming that eight of the nine oxygen atoms in the CaU_3O_9 cell are at the normal UO_2 sites and neglecting the 9th

TABLE 1 COMPARISON BETWEEN OBSERVED INTENSITIES OF HIGH PRESSURE CaU_3O_9 REFLEXIONS AND CALCULATED INTENSITIES FOR Cu_3Au TYPE ORDERING OF Ca AND U CATIONS

d (Å)	Index	I_{obs}	I_{calc}	Nature of reflexion
5 36	100	25	18	Superlattice
3 79	110	15	17	Superlattice
3 101	111	100	100	UO_2
2 677	200	50	37	UO_2
2 399	210	15	10	Superlattice
2 200	211	10	8	Superlattice
1 899	220	60	50	UO_2
1 784	300, 221	10	6	Superlattice
1 703	310	5	4	Superlattice
1 620	311	50	47	UO_2
1 551	222	20	10	UO_2
1 489	320	5	3	Superlattice
1 436	321	5	5	Superlattice
1 343	400	20	10	UO_2
1 303	410, 322	5	4	Superlattice
1 264	411, 330	5	3	Superlattice
1 232	331	30	26	UO_2
1 203	420	20	19	UO_2
1 159	421	5	4	Superlattice
1 144	332	5	2	Superlattice
1 096	422	20	26	UO_2

oxygen atom, the intensities in the CaU_3O_9 diffraction pattern with Cu_3Au type ordering were calculated taking into account the Lorentz-polarization correction but neglecting absorption effects Calculated and observed intensities are shown in Table 1 The observed intensities were estimated visually The degree of agreement between calculated and observed intensities would appear to warrant the assumption of Cu_3Au type ordering of uranium and calcium ions in the high pressure CaU_3O_9

To determine the possible effect of oxygen content on ordering in CaU_3O_{8+x} type compounds, a series of mixtures with nominal compositions $CaU_3O_{7\ 75}$, $CaU_3O_{8\ 40}$, and $CaU_3O_{8\ 80}$ were prepared by mixing U_4O_9, U_3O_8, and CaO in the proper proportions The first three of the high pressure samples were face-centred-cubic without extra reflexions Presumably in these materials CaO was dissolved in the UO_{2+x} lattice without ordering of the Ca and U ions In high pressure $CaU_3O_{8\ 80}$, which was ordered, there was no observable decrease in intensity of the superlattice reflexions as compared with CaU_3O_9 samples

To determine whether the ordering was pressure dependent, samples of the CaU_3O_9 mixture were reacted at 1 atm pressure in argon at 800, 1000 and 1200°C In all instances, face-centred reflexions were present without superlattice reflexions In the 800 and 1000°C samples, there were also weak U_3O_8 reflexions indicating incomplete reaction

An approximate value of the electrical resistivity of the ordered CaU_3O_9 was obtained using a Bridgman anvil apparatus in which only a small sample is required [(4)] The resistivity was approximately 100 ohm cm A U_4O_9 sample had nearly the same resistivity

Effects of high pressure on mixtures with nominal composition $CaUO_x$ were also investigated High pressure samples with nominal composition $CaUO_3$ and $CaUO_{3\ 67}$ were apparently face-centred-cubic with lattice parameters $a_0 = 5\ 38$ Å and 5 37 Å respectively A 1 CaO 1 UO_3 mixture reacted at high pressure to form the rhombohedral calcium uranate, $CaUO_4$, described by ZACHARIASEN [(5)]

The powder pattern of the high pressure $CaUO_3$ sample was carefully examined for weak reflexions to determine whether it was actually face-centred-cubic A Type C $CaUO_3$ compound has been reported [(6)] The strongest reflexions in Type C compounds coincide with those of a fluorite structure with one-half the cubic cell dimension However, there are many visible nonfluorite reflexions in Type C compounds It is quite certain that the high pressure $CaUO_3$ was not Type C, since none of the extra reflexions ordinarily present in the Type C pattern were observed The high pressure $CaUO_3$ probably was a solid solution of CaO in the UO_2 structure

High pressure samples with nominal CdU_3O_9 composition were face-centred-cubic with lattice parameter a 5 39 Å No superlattice reflexions were visible If Cu_3Au type ordering were present in CdU_3O_9, the calculated intensities without absorption correction of the (100) and (110) reflexions, which are the strongest superlattice reflexions, would be six and five compared to 100 for the (111) reflexion The superlattice reflexions would be considerably weaker in CdU_3O_9 than in CaU_3O_9 It is possible that the low angle (100) and (110) reflexions would be too weak to observe because of the high uranium absorption While there was no positive evidence for ordering in the high pressure CdU_3O_9, the possibility cannot be ruled out on the basis of the present limited experiments.

---

(4) A P YOUNG, W B WILSON and C M SCHWARTZ *Phys Rev* **121**, 77 (1961)

(5) W H ZACHARIASEN, *Acta Cryst* **1**, 281 (1948)

(6) K B ALBERMAN, R C BLAKEY and J S ANDERSON, *J Chem Soc* 1352 (1951)

The behaviour of $CdUO_x$ samples under pressure was the same as that of $CaUO_x$ samples. $CdUO_3$ and $CdUO_{3.67}$ samples were face-centred-cubic. The high pressure $CdUO_4$ exhibited a diffraction pattern nearly identical to that of the rhombohedral calcium uranate.

DISCUSSION

The ordering in high pressure CaU_3O_9 compounds is apparently the first instance of Cu_3Au type ordering of cations in a mixed oxide. Attempts to produce at ambient pressure either CuAu or Cu_3Au type ordering in the cation lattice in solid solutions of NiO, FeO and MnO in MgO have been made by WILSON,(7) so far without success. The possibility of producing ordered structures in binary uranium oxide–metal oxide solid solutions has been mentioned by HOEKSTRA and PARKER.(8)

Ordering of the cations in a mixed oxide such as CaU_3O_9 would depend on both cation–cation and cation–anion interaction. The dependence of ordering on oxygen content in CaU_3O_{8+x} compounds indicates that the ordering is closely related to Ca–O and U–O bonding. CaU_3O_{8+x} may be simply related to the fluorite structure if the added oxygen ions are located at the centres of R_4O_8 fluorite cells with cations at cell corners and face centres. In R_4O_9, all the cell centres would be occupied by oxygen. The corner sites in the resulting R_4O_9 unit cell would be differentiated from the face-centred sites with respect to R–O bonding. The oxygen ions at cell centres would be distant $0.866a_0$ from the corner cations and would be separated from them by other oxygen ions on the body diagonal. The separation between the cell-centred oxygen and the face-centred cations would be $0.500a_0$. Most of the bonding from the cations to the interstitial cell-centred oxygen would be from the face-centred cations. The corner cation sites in CaU_3O_9 might be preferred by calcium, since the bonding would resemble that of the 8:4 co-ordinated fluorite structure. Location of calcium at corners and uranium at face centres of the cells with interstitial oxygen at cell centres would result in Cu_3Au type ordering of the cation lattice.

With $a_0 = 5.37$ Å, the distance of closest approach of the oxygen ions in this structure would be 2.32 Å. This is closer than normal proximity for oxygen ions. This may account for the fact that the ordered CaU_3O_9 is a high pressure material. The distance of closest oxygen approach in other high pressure compounds is less than normal. For instance, in stishovite, the high pressure rutile-type SiO_2, and in the high-pressure rutile-type $AlAsO_4$, the distance of closest approach of oxygen ions is 2.23 Å and 2.34 Å respectively.(9)

The variation of the fluorite structure in which oxygen ions are located at centres of R_4O_8 fluorite cells with cations at the corners was once proposed for U_4O_9.(10) However, neutron diffraction analysis and observations of certain superlattice reflexions by BELBEOCH *et al.*, indicated that the extra oxygen ions in U_4O_9 are permuted among four equivalent sites in fluorite-type cells with oxygen at the corners.(11) If the oxygen lattice in CaU_3O_9 resembled that of U_4O_9 and if the positions of Ca and U ions were dependent on anion–cation bonding, the calcium ions would also permute among equivalent sites and the same superlattice reflections observed by Belboech would be observed In fact the superlattice reflections in U_4O_9 and in the ordered CaU_3O_9 are entirely different It is reasonable to assume therefore, that the oxygen lattice in the high pressure CaU_3O_9 does not resemble the U_4O_9 oxygen lattice but is the simple modification of the UO_2 oxygen lattice earlier proposed for U_4O_9

---

(7) H. W. WILSON, Aeronautical Systems Div. Tech. Rept. 61–92 (June, 1961).

(8) H. R. HOEKSTRA and H. S. PARKER, Uranium Oxide: Properties and Applications, Naval Reactors Div. of Reactor Dev., pp. 271–299. USAEC (1961).

(9) A. P. YOUNG, C. B. SCLAR and C. M. SCHWARTZ, *Z. Krist.* **118**, 223 (1963).

(10) H. HERING and P. PERIO, *Bull. Soc. Chim. France* **19**, 351 (1952).

(11) B. BELBEOCH, C. PIEKARSKI and P. PERIO, *Acta Cryst.* **14**, 837 (1961).

Neutron diffraction might be useful in determining more definitely the oxygen positions in the high pressure CaU_3O_9 Some of the high pressure CaU_3O_9 samples were coarsely crystalline It is possible that single crystals large enough for neutron diffraction might be grown by the use of controlled temperature gradients and the addition of water or some other mineralizer in the high pressure capsule

It was thought that the electrical resistivity of CaU_3O_9 would be higher than that of U_4O_9 because of blocking action of Ca ions Actually there was little difference in the resistivity of U_4O_9 and CaU_3O_9 Assuming that Ca is always divalent, U must have at least two valences in CaU_3O_9 with two-thirds U^{5+} and one-third U^{6+} as one possibility Conductivity can occur by hopping transport between adjacent uranium ions of different valence in a manner similar to that proposed for Fe_3O_4 (12)

In the fully oxidized state, $CaUO_x$ high pressure compounds have the $CaUO_4$ calcium uranate structure Partially oxidized compounds are face-centred-cubic with lattice parameter reduced from that of UO_2 Similar results have been reported at ambient pressure (8)

The fully reduced pressure compound $CaUO_3$ is also face-centred-cubic This is in contrast to the type C $CaUO_3$ formed in vacuum at very high temperature (6) There were no superlattice reflexions indicative of any ordering of U and Ca ordering in the high pressure $CaUO_3$ It would be of interest to know where the oxygen ions are located in this material, which is so defective in anions compared with a fluorite-type compound For this analysis, neutron diffraction would probably be required

Acknowledgements –The authors would like to acknowledge the assistance of P B ROBBINS in the experimental work, and of A F AUSTIN for helpful discussions and suggestions

(12) D S TANNHAUSER, *J Phys Chem Solids* **23**, 25 (1962)

J. Inorg. Nucl. Chem. 1963. Vol. 25. pp. 1139 to 1140. Pergamon Press Ltd. Printed in Northern Ireland

KINETICS OF THE IRON (II)-IRON (III) ELECTRON EXCHANGE REACTION IN ICE MEDIA

R. A. Horne
Arthur D. Little, Inc., Acorn Park, Cambridge, Mass.

(*Received* 11 *October* 1962; *in revised form* 4 *March* 1963)

Abstract—Electron-exchange has been observed between cations in ice media. The overall reaction rate constant for the Fe(II)–Fe(III) electron-exchange reaction at −78°C in the eutectic frozen from an aqueous solution initially 0.55 M in $HClO_4$ is $2.1 \pm 0.3 \times 10^{-3}$ $sec^{-1}M^{-1}$. As in liquid water the process is first order in each reactant. The rate is the same in the presence of chloride ion as in the presence of perchlorate ion. The rate decreases with increasing acidity. The results indicate that electron-transfer can occur over very great distances in aqueous media by a water-bridging mechanism.

Some time ago Dodson and Davidson(1) discussed the possibility that the mechanism of the Fe(II)–Fe(III) electron-exchange reaction might involve electron-transfer via the solvent molecules in aqueous media. Subsequently Reynolds and Lumry(2) and Klotz, *et al.*(3) suggested that the reaction might proceed via a Grotthuss type mechanism involving hydrogen transport along extended bridges of suitably oriented water molecules. The importance of the role of solvent in electron-exchange has also been recognised by Libby,(4) Weiss,(5) Platzman and Frank,(6) and Marcus.(7) Experiments in heavy water(8, 9, 10) and in non-aqueous and mixed solvent media(11, 12, 13) while yielding evidence which appears to give the water bridging theory support, have not given any information which alone provides a basis for distinguishing unambiguously whether the Fe(II)–Fe(III) exchange proceeds by a complex anion bridging or water-bridging mechanism.

EXPERIMENTAL

The materials used, the preparation of the stock solutions and the methods of analysis have been described in detail by Silverman and Dodson.(14) The radioactive $Fe(ClO_4)_3$ solution was prepared from $^{59}Fe\ Cl_3$ HCl solution obtained from Oak Ridge National Laboratory.

---

(1) R. W. Dodson and N. Davidson, *J. Phys. Chem.* **56**, 855 (1952) (See discussion).

(2) W. L. Reynolds and R. W. Lumry, *J. Chem. Phys.* **23**, 2460 (1955).

(3) I. M. Klotz, J. Ayers, J. Y. C. Ho, M. G. Horowitz and R. E. Heiney, *J. Amer. Chem. Soc.* **80**, 2132 (1958).

(4) W. F. Libby, *J. Phys. Chem.* **56**, 863 (1952).

(5) J. Weiss, *J. Chem. Phys.* **19**, 1066 (1951).

(6) R. Platzman and J. Frank, *Physik* **138**, 411 (1954).

(7) R. A. Marcus, *J. Chem. Phys.* **24**, 966 (1956); **26**, 867, 872 (1957).

(8) D. Bunn, F. S. Dainton and S. Duckworth, *Trans. Faraday Soc.* **55**, 1267 (1959).

(9) J. Hudis and R. W. Dodson, *J. Amer. Chem. Soc.* **78**, 911 (1956).

(10) N. Sutin, J. K. Rowley and R. W. Dodson, *J. Phys. Chem.* **65**, 1248 (1961).

(11) R. A. Horne Ph.D. Thesis, Columbia (1955).

(12) N. Sutin, *J. Phys. Chem.* **64**, 1766 (1960).

(13) A. G. Maddock, *Trans. Faraday Soc.* **55**, 1268 (1959).

(14) J. Silverman and R. W. Dodson, *J. Phys. Chem.* **56**, 846 (1952).

The conduct of the experiments and the separation procedure were similar to those described by SILVERMAN AND DODSON(14) Two solutions, both 10 ml in volume were prepared They were of the same ionic strength and concentration of added anions, but one contained the tagged Fe(III) perchlorate and the other the Fe(II) perchlorate Both solutions were chilled at 0 C Five reaction mixture samples were prepared next by adding 1 ml of each solution to small test tubes stoppering the tubes, shaking well and rapidly, and immediately immersing in a dry-ice acetone bath (78 C) Freezing was complete in less than 30 sec A dry-ice-chloroform bath was used for the −67 C runs, a dry-ice carbon tetrachloride bath for the runs at 23 C At regular time intervals, one of the tubes was removed from the bath, quickly crushed, and tube and contents dumped into a room temperature quenching solution of α,α-dipyridyl buffered with sodium acetate to give a pH of 5 Next the Fe(III) was precipitated as the hydroxide by adding excess NH_4OH The mixture was filtered through a sintered glass filter using a suspension of $CaCO_3$ in conc NH_4OH as a filtering aid A sample of the filtrate containing the Fe(II) was counted as a solution in a Nuclear-Chicago well-type scintillation counter Efforts to dissolve and count the Fe(III) precipitate did not give reproducible results

In runs at 0 C the two 10 ml solutions were mixed and 2 ml liquid samples pipetted off at regular time intervals

RESULTS

The overall reaction rate constant, k

$$\text{Rate} = k(\text{Fe(II)})(\text{Fe(III)}) \tag{1}$$

was calculated from half-lives $t_{1/2}$ determined from McKAY plots and the expression

$$k = 0.693/[(\text{Fe(II)}) + (\text{Fe(III)})]t_{1/2} \tag{2}$$

as described by SILVERMAN and DODSON (14) Activities were corrected for the decay of the ^{59}Fe As might be expected, the induced exchange was greater in the present experiments in ice than in earlier studies in liquid water (11–14) The experimental error, estimated from the maximum spread of the points in the McKAY plots, was 20 per cent Typical McKAY plots are shown in Fig 1 At −78° C the exchange runs were followed for as long as 52 hr (not shown in Fig 1) Attempts to follow the exchange for even longer periods of time were frustrated by the onset of erratic results for which spectrophotometric analysis showed the slow oxidation of the Fe(II) to be responsible

As the reaction mixture freezes, relatively pure ice separates out and the remaining electrolyte solution becomes more concentrated until the eutectic temperature is reached, whereupon, as shown by separate experiments, the composition remains constant, and the still-liquid solution solidifies A corrected overall rate reaction constant, k', was calculated from

$$k' = 0.693/C\{[\text{Fe(II)}] + [\text{Fe(III)}]\}t_{1/2} \tag{3}$$

where C is the ratio of concentration of the principal electrolyte component in liquid solution at the eutectic to the initial concentration before freezing The former value was calculated from the freezing curves of the appropriate system

A separate experiment was performed to test for any further segregation of iron species in the eutectic mixture An aqueous $HClO_4$ solution of the same composition as the eutectic and containing Fe(III) was slowly frozen Before solidification was complete, samples of the solid and of the remaining liquid were removed Spectrophotometric analysis showed that the Fe(III) concentrations in the solid, liquid, and in the original liquid solution were all the same, indicating no further macroscopic segregation of the iron species upon solidification of the eutectic No evidence was observed for microscopic segregation of a concentrated solution or crystals of (a) a single valence state of iron, (b) one valence state of iron contaminated with the other

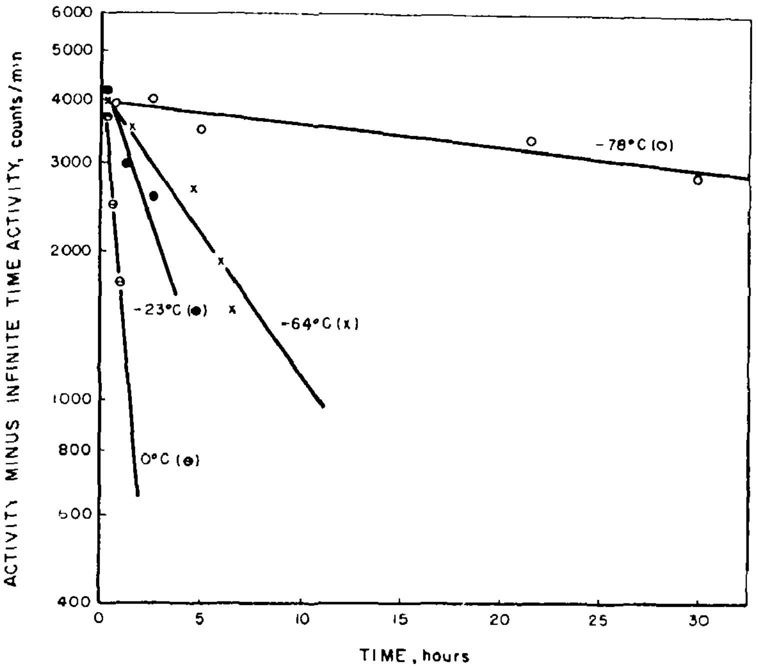


FIG 1 —McKAY plots for the iron (II) iron (III) electron-exchange reaction at 0, 23 64 and 78 C

valence state, or (c) a mixed salt containing both valence states in roughly equal amounts Situation (a) would represent a separation of the reactants and would result in no or exceedingly slow exchange, situation (b) would result in a large induced exchange and incomplete reaction, and, situation (c) would result in rapid exchange, the exchange probably being complete within the time of mixing (i e 100 per cent induced exchange) None of these possible results were obtained in particular, although the induced exchange in the present experiments was somewhat larger than in similar exchange experiments at higher temperatures, the amount of induced exchange was well within the limits calculated from the estimated freezing and thawing times

As a check upon the techniques used, a number of experimental runs were made in liquid, aqueous $HClO_4$ media at 0 C The results (Table 1) are in good agreement with values reported by earlier investigations A number of runs were made at 78 C, the lowest temperature studied Since this temperature is well below --58 C, the eutectic temperature of the H_2O-$HClO_4$ system, the medium is solid The results are summarized in Table 2 The constancy of the overall reaction rate constant, even though the relative concentration of the reactants was varied, justified the assumption that at low temperatures the reaction continues to be first order with respect to both reactants These same kinetics have been found to obtain in liquid aqueous media in the presence of all anions hitherto studied(11 14 15 16 17) and in ethanolic media (11)

The rate of the Fe(II)-Fe(III) electron exchange was also measured at −22 and

---

(15) J HUDIS and A C WAHL, *J Amer Chem Soc* **75**, 4153 (1957)
(16) G S LAURENCE, *Trans Faraday Soc* **53**, 126 (1957)
(17) R A HORNE *J Phys Chem* **64**, 1512 (1960)

TABLE 1. RATE OF THE Fe(II)-Fe(III) ELECTRON-EXCHANGE REACTION IN AQUEOUS 0.55 M $HClO_4$ MEDIA AT 0.0°C

$HClO_4$ Conc (M)	Ionic strength	Fe(II) conc (M)	Fe(III) conc (M)	Half-life $t_{1/2}$ (sec)	Reaction rate constant (sec^{-1} $mole^{-1}$)
0.55	0.55	13.5×10^{-5}	6.0×10^{-6}	3.30×10^{3}	1.48
0.55	0.55	13.5×10^{-5}	6.0×10^{-6}	2.94×10^{3}	1.24
0.55	0.55	13.5×10^{-5}	6.0×10^{-6}	3.06×10^{3}	1.60
0.55	0.55	6.50×10^{-5}	6.00×10^{-6}	6.78×10^{3}	1.44
					1.44 ± 0.10
0.55	0.55	SILVERMAN AND DODSON(11)			1.35
0.40	0.50	HUDIS AND WAHL(15)			1.48
0.55	0.55	HORNE(17)			1.31

TABLE 2. RATE OF Fe(II)-Fe(III) ELECTRON-EXCHANGE REACTION IN SOLID AQUEOUS $HClO_4$ MEDIA AT −78°C

Temperature (°C)	Initial concentrations Fe(II) M	Initial concentrations Fe(III) M	Half-life $t_{1/2}$ sec	Overall reaction rate const k sec^{-1} M^{-1}	Final concentrations Fe(II) (M)	Final concentrations Fe(III) (M)	k' sec^{-1} $mole^{-1}$
−78	13.5×10^{-5}	5.5×10^{-6}	180,000	2.7×10^{-2}	16.9×10^{-4}	6.9×10^{-5}	2.3×10^{-3}
−78	13.5×10^{-5}	5.5×10^{-6}	241,000	2.0×10^{-2}	16.9×10^{-4}	6.9×10^{-5}	1.6×10^{-3}
−78	4.6×10^{-5}	5.5×10^{-6}	385,000	3.4×10^{-2}	5.8×10^{-4}	6.9×10^{-5}	2.7×10^{-3}
−78	6.5×10^{-5}	5.5×10^{-6}	490,000	2.3×10^{-2}	8.1×10^{-4}	6.9×10^{-5}	1.8×10^{-3}
−78	6.5×10^{-5}	5.5×10^{-6}	222,000	2.6×10^{-2}	8.1×10^{-4}	6.9×10^{-5}	2.1×10^{-3}
				$2.6 \pm 0.4 \times 10^{-2}$			$2.1 \pm 0.3 \times 10^{-3}$

(Initial Concentration of $HClO_4$ = 0.55 M)
(Initial Ionic Strength = 0.55)

TABLE 3.—TEMPERATURE DEPENDENCE OF THE RATE OF THE Fe(II)-Fe(III) ELECTRON EXCHANGE REACTION IN AQUEOUS 0.55 M $HClO_4$ MEDIA*

Temp (°C)	State	Initial concentrations Fe(II)	Initial concentrations Fe(III)	Half-life $t_{1/2}$ sec	Overall reaction rate constant k (sec^{-1} $mole^{-1}$)	Overall reaction rate constant k' (sec^{-1} $mole^{-1}$)
21.6	L				9.97	9.97
14.7	L	Data of SILVERMAN AND DODSON(11)			5.34	5.34
7.3	L				2.73	2.73
0.0	L	Average from Table 1			1.44	1.44
−22	L + S	6.5×10^{-5}	5.5×10^{-6}	9.4×10^{3}	1.03	0.14
−23	L + S	1.35×10^{-4}	5.5×10^{-6}	7.6×10^{4}	0.65	0.088
−64	S	1.35×10^{-4}	5.5×10^{-6}	2.2×10^{4}	0.22	0.018
−64	S	6.5×10^{-5}	5.5×10^{-6}	8.9×10^{4}	0.11	8.7×10^{-3}
−78	S	Average from Table 2			2.6×10^{-2}	2.1×10^{-3}

* Initial concentration

−23°C, and −64°C. These results, together with the −78°C results and earlier work of SILVERMAN and DODSON,(14) are summarized in Table 3 to give a total temperature range of +22 to −78°C.

The overall reaction rate constant of the reaction at −78°C in a medium initially 0.55 M in HCl was measured and found to be 1.9 × 10^{-3} sec^{-1} mole^{-1} after correcting for electrolyte concentration upon freezing. Within experimental error, this value is the same as for $HClO_4$. (See Table 2.)

The acid dependence of the reaction rate was also investigated at −78°C. The results are summarized in Table 4. Inasmuch as the phase diagram for the ternary system $HClO_4$–$NaClO_4$–H_2O is not known, attempts to try to make an electrolyte concentration correction is probably not worth while in those cases where $HClO_4$ and $NaClO_4$ were present in comparable amounts.

TABLE 4.—ACID DEPENDENCE OF THE RATE OF THE Fe(II)–Fe(III) ELECTRON-EXCHANGE REACTION IN ICE MEDIA AT −78°C

Initial electrolyte concs.		Initial concentration		Half life	Overall reaction rate constant	
$HClO_4$ (M)	$NaClO_4$ (M)	Fe(II)	Fe(III)	$t_{1/2}$ sec	k (sec^{-1} mole^{-1})	k' (sec^{-1} mole^{-1})
0.55	0.00	Average from Table 2			2.6 × 10^{-2}	2.1 × 10^{-3}
0.275	0.275	1.35 × 10^{-4}	5.5 × 10^{-6}	1.08 × 10^{1}	4.6 × 10^{-2}	
0.003	0.53	1.35 × 10^{-4}	5.5 × 10^{-6}	5.4 × 10^{1}	9.1 × 10^{-2}	4.8 × 10^{-3}

DISCUSSION

In the presence of a complexing anion, X^{-m}, the rate of the Fe(II)–Fe(III) electron exchange reaction can be presented by(18)

$$R = \sum_{x}\sum_{n=0} k_{x,n}(FeX_n^{3-mn})(Fe^{2+}) \tag{4}$$

which is valid for all catalysing anions hitherto studied for values of n up to at least two. In chloride media (4) becomes

$$R = k_0(Fe^{3+})(Fe^{2+}) + k_{1,OH}(FeOH^{2+})(Fe^{2+}) + k_{1,Cl}(FeCl^{2+})(Fe^{2+}) + k_{2,Cl}(FeCl_2^{+})(Fe^{2+}) + \dots \tag{5}$$

Using values of the specific reaction rate constants and hydrolysis and complex formation constants used or measured by SILVERMAN and DODSON(14) and extrapolating to −78°C, one finds that the contribution of chloride complexes to the exchange has become negligible, a conclusion in agreement with the observation that at this temperature, the overall specific reaction constant is the same in aqueous HCl as in aqueous $HClO_4$.

The results in Table 4 show some acid dependency indicating that the

$$k_{1,OH}(FeOH^{2+})(Fe^{2+})$$

term in Equation (5) is still making a contribution at −78°C. The acid effect, however, is very much less than at 0°C. When the proton concentration is reduced from 0.55 to 0.003 M, the overall reaction rate constant doubles, while at 0°C, SILVERMAN and DODSON(14) found a twelve fold increase in going from 0.55 to 0.016 M.

---

(18) R. A. HORNE, *Nature, Lond.* **181**, 410 (1958).

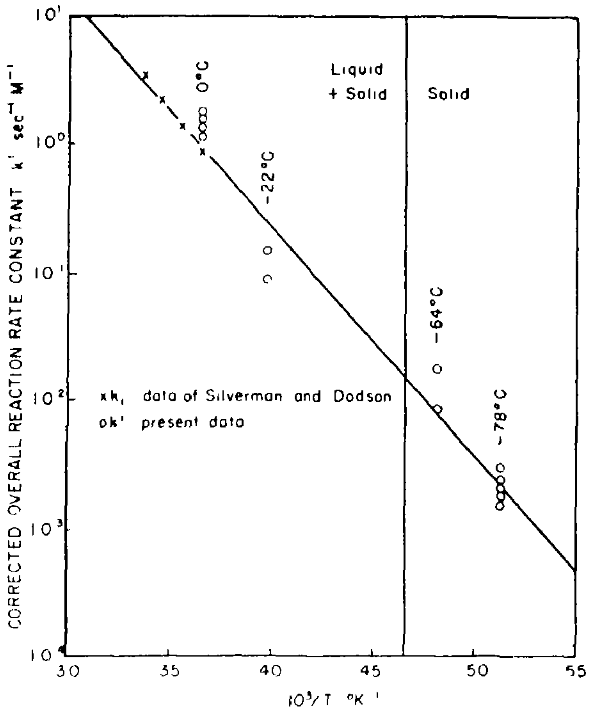


FIG. 2 - Temperature dependence of the iron (II) iron (III) electron exchange reaction

In Fig 2, the corrected overall reaction rate constant is plotted on a logarithmic scale vs the reciprocal of the absolute temperature Values of the specific reaction rate constant, k, as determined by SILVERMAN and DODSON[14] are also plotted By substituting into the integrated form of the Arrhenius Equation

$$\frac{d(\ln k')}{dT} = \frac{E_a}{RT^2} \tag{6}$$

one finds that the slope of the resulting straight line corresponds to an activation energy of 8.4 kcal/mole which is in good agreement with values reported earlier and summarized by HALPERN [19]

A very important feature of the curve in Fig 2 is the absence of any discontinuity or break at −58°C, the eutectic temperature, as the remaining electrolytic solution freezes The absence of such a feature suggests (a) there is no change in mechanism as one proceeds from a liquid to a solid medium, (b) the rate of the reaction is not diffusion controlled, and (c) if the mechanism of the electron-exchange is related to the mechanism of proton mobility, then the proton mobility must, apart from a temperature effect, be the same in ice as in liquid water

LAIDLER[20] has suggested that the Fe(II)-Fe(III) electron-exchange reaction in aqueous media is a diffusion-controlled process In the absence of any information to the contrary (such as a change in order or change in the temperature dependence of the rate), it is reasonable to assume that the mechanism of the rate-controlling step of the Fe(II)-Fe(III) exchange process does not generically differ in liquid water and

[19] J HALPERN, *Quart Revs* **15**, 207 (1961) (See Table 1, p 211)

[20] K J LAIDLER, *Canad J Chem* **36**, 138 (1959)

in ice. Unfortunately, there is a paucity of information concerning the diffusion rates of highly solvated polyvalent cations and their complex ions in both liquid water and ice. LAIDLER(20) uses a value of 1.2×10^{-5} cm² sec⁻¹ for the diffusion constant of ferrous and ferric ions in water of 25°C. Their diffusion constants in ice are not known.

We have performed a simple diffusion experiment in which we tried to detect movement in a pure ice-frozen $FeCl_3$ solution boundary at −78°C. In sixty days, the boundary moved less than 0.5 cm, thus indicating that the diffusion constant of Fe(III) chloride complex ions is less than 10^{-7} cm² sec⁻¹.

The self-diffusion of water in liquid water and in ice has been measured,(21,22,23) however, and the ratio of the diffusion constants is

$$\frac{D_{H_2O\ l\ 25^\circ C}}{D_{H_2O\ s\ 0^\circ C}} = \frac{2.4 \times 10^{-5}}{1.0 \times 10^{-10}} = 2.4 \times 10^5 \tag{7}$$

The ratio of the diffusion constants of hydrated Fe(II)–Fe(III) species in water and ice should be greater than the above ratio for the self-diffusion of water, especially if the ice is at −78°C, rather than 0°C. For solid-state diffusion in metals,(24) D ranges around 10^{-10} cm² sec⁻¹ and is sometimes as small as 10^{-17} cm² sec⁻¹. The present process in ice should be of comparable or even greater slowness, thus 10^{-15} cm² sec⁻¹ does not appear to be an unreasonable estimate for the diffusion constant of highly solvated cations in ice. Such an estimate leads to a value of roughly 10^{10} for the ratio $D_{Fe(II)\ or\ Fe(III)\ water\ 25^\circ C}$ to $D_{Fe(II)\ or\ Fe(III)\ ice\ -78^\circ C}$. The rate constant of a reaction is proportional to the sum of the diffusion coefficients of the reactants.(20) If the electron-exchange is diffusion controlled, the ratio of the reaction rate constants in water and ice should be equal to the corresponding diffusion coefficient ratio. The present experiments show that such is not the case.

$$\frac{k_{water\ 25^\circ C}}{k_{ice\ -78^\circ C}} \approx 5 \times 10^3 \tag{8}$$

Protons have an anomalously high apparent mobility in liquid aqueous solution, and this phenomenon has been attributed to a Grotthuss type mechanism.(25) An ordered lattice is expected to facilitate this process; therefore, it has been suggested that the anomalous mobility of protons in ice should be very great,(26,27,28,29) 0.1–0.5 cm² sec⁻¹ V⁻¹. HEINMETS(30) has made direct measurements of proton mobilities in protonated ice and obtained values ranging from 2.0×10^{-5} cm² sec⁻¹ V⁻¹ at −20°C to 2.2×10^{-4} cm² sec⁻¹ V⁻¹ at 15°C. That is to say, apart from the temperature dependence, he has found that proton mobilities in ice are comparable to those in liquid water. If both the anomalous mobilities of protons and the Fe(II)–Fe(III)

---

(21) A. W. ADAMSON and R. R. IRANI, *J. Amer. Chem. Soc.* **79**, 2969 (1957).

(22) W. KUHN and M. THURKAUF, *Helv. Chim. Acta* **41**, 938 (1958).

(23) D. C. DOUGLASS and D. W. MCCALL, *J. Chem. Phys.* **31**, 569 (1959).

(24) C. J. SMITHELLS, *Metals Reference Book*, Vol. 2, pp. 551 *et seq.* Interscience, New York (1955).

(25) E. HUCKEL, *Z. Elektrochem.* **34**, 546 (1928).

(26) M. EIGEN and L. DEMAEYER, *Z. Elektrochem.* **60**, 1037 (1956).

(27) B. E. CONWAY and J. O'M. BOCKRIS, *J. Chem. Phys.* **28**, 354 (1958).

(28) M. EIGEN and L. DEMAYER, *Proc. Roy. Soc.*, **247**, A, 505 (1958).

(29) B. E. CONWAY, *Canad. J. Chem.* **37**, 178 (1959).

(30) F. Heinmets, *Nature, Lond.* **188**, 925 (1960).

electron-exchange reaction arise from the same mechanism, possibly of a Grotthuss-type as suggested by Reynolds and Lumry,[2] and if the process is greatly facilitated in ice, one might expect an abrupt increase in rate as the solution freezes Figure 2 fails to show any break, and thus the present results appear to support the findings of Heinmets [30] However, it should be cautioned that the present experiments and those of Heinmets[30] necessarily involved highly impure ice Furthermore, in the present experiments, the solutions were rapidly frozen, hence, the resulting ice is probably relatively disordered

In the present experiments, there are more than 3000 water molecules for each Fe(II) Fe(III) species Estimates based on the concentrations involved indicated that in the solid medium, the reactants are separated by distances of roughly 100 Å This finding is to be compared with the earlier conclusion of Hudis and Wahl[15] that the distance between iron nuclei in the transition state in the case of the fluoride catalysed exchange is large enough to accommodate one or more water molecules, and of Horne[11] that the apparent dielectric constant of the medium which the reactants see is that of water, even in ethanolic solutions quite dilute in water

The ability of redox processes to occur over great distances through aqueous electrolytic solutions by water bridges may have considerable significance in explaining the mechanistic details of certain biologically important processes The electrical properties of hydrated hemoglobin[31] and the differences in oxidative susceptibility of free heme and hemoglobin in aqueous solution[32] may be due to Grotthuss-like transport processes Klotz *et al*[3] have theorized that a number of important long-range biological electron-transfer processes might occur via water bridges

Acknowledgements -The author wishes to express his gratitude to the Research Projects Committee of Arthur D Little, Inc for funding the present work, to Drs A G Emslie, G R Frysinger, J H B George, H O McMahon, E S Shanley of A D Little Inc and Dr F Heinmets of the Quartermaster Research and Engineering Cen, Natick, for their helpful discussions, and to Miss F Sullivan for assistance with the experiments

[31] D D Eley and D I Spivey, *Nature Lond* **188**, 724 (1960)

[32] R A Horne, *Science* **130**, 164 (1959)

J Inorg Nucl Chem 1963 Vol 25 pp 1147 to 1154 Pergamon Press Ltd Printed in Northern Ireland

SPECTROPHOTOMETRIC STUDIES ON PROTONATED, AMMINO AND HYDROXO COMPLEXES OF COPPER (II), NICKEL (II) AND COBALT (II) VERSENATES

T R BHAT and M KRISHNAMURTHY
Chemistry Division, Atomic Energy Establishment, Trombay, India

(*Received* 3 *December* 1962)

Abstract –The formation of mixed complexes of the type MY X, where M Cu(II), Ni(II) and Co(II), Y EDTA, and X H_2O, NH_3 and OH^-, were spectrophotometrically identified and their formation constants determined

THE normal 1 1 complexes of ethylene diamine tetra-acetic acid (versene, EDTA,Y) with copper (II), nickel (II) and cobalt (II) have been studied by several workers(1 4), but very little data has appeared on the stability of mixed EDTA complexes of these metals SCHWARZENBACH reported(5) from a qualitative study of colour changes, the existence of mixed complexes of the type MY X, where M= Cu(II), Ni(II), Co(II), etc, and X H_2O, NH_3, OH^-, etc, and spectrophotometrically determined the formation constant of one of the complexes, viz, CoY CNS^3

Copper (II), nickel (II) and cobalt (II) have been used successfully as retaining ions in the ion exchange separation of rare earths using EDTA as eluant A detailed study of the mixed EDTA complexes of these elements was found necessary for elucidation of the mechanism of separation of rare earths by ion exchange

EXPERIMENTAL

1 *Materials and methods*

The EDTA employed was purified by recrystallization of the E Merck, metal titration grade, Titriplex III, from deionized water It was then standardized by titration against zinc chloride solution using Erio T as indicator(6) Sodium perchlorate was prepared by neutralizing (pH-measurements), perchloric acid solution with carbonate-free hydroxide To prepare the metal perchlorates, the corresponding nitrates were precipitated as hydroxides, washed free from soluble salts and dissolved in perchloric acid The salts were further purified by double crystallization and finally the solutions were standardized by titration against EDTA (6) The metal EDTA complexes were obtained by mixing the standard metal perchlorates and disodium EDTA in the mole ratio 1 1 The ionic strength was adjusted to $\mu = 1$ by addition of sodium perchlorate All the pH adjustments were made by addition of either perchloric acid or of sodium hydroxide The concentration of the complex in the final solution was kept in the range 0 005 0 015 M depending upon the molar absorbance The pH

---

(1) G SCHWARZENBACH, R GUT and G ANDEREGG, *Helv Chim Acta*, **37**, 937 (1954)

(2) V L HUGHES and A E MARTELL, *J Phys Chem* **57**, 694 (1953)

(3) G SCHWARZENBACH and E FREITAG, *Helv Chim Acta*, **34**, 1503 (1951)

(4) A E MARTELL and R C PLUMB, *J Phys Chem* **56**, 993 (1952)

(5) G SCHWARZENBACH, *Helv Chim Acta* **32**, 839 (1949)

(6) G SCHWARZENBACH, *Complexometric Titrations* (translated to English by H IRVING) Methuen and Co, London (1957)

was calibrated at the same ionic strength ($\mu = 1$) with standard solutions of perchloric acid and sodium hydroxide.

The solutions were brought to equilibrium at 25°C and the temperature in the spectrophotometer cell was in the range 25 ± 1°C. All the absorption measurements were made with a Beckman model DU spectrophotometer using 1 cm quartz cells. The pH measurements were made with a Beckman model G pH meter.

2. *Calculation of stability constants*

(a) *Formation constant of the protonated complex.* The concentration of YH^{3-} in solution is related to the total free EDTA concentration, ΣY, ($\Sigma Y = Y^{4-} + YH^{3-} + YH_2^{2-} + YH_3^{-} + YH_4$) by the expression,

$$[YH^{3-}] = \frac{K_4\Sigma Y(H^+)}{1 + K_4(H^+) + K_3K_4(H^+)^2 + K_2K_3K_4(H^+)^3 + K_1K_2K_3K_4(H^+)^4} \tag{1}$$

where K_1, K_2, K_3 and K_4 are reciprocals of successive dissociation constants of YH_4. The K_n values for EDTA at 25°C and $\mu = 1$, has been reported by MARTELL and CARINI[7] as, $\log K_1K_2 = 5.0$*, $\log K_3 = 6.35$ and $\log K_4 = 9.3$.

It was observed that under the experimental conditions Beer's law was obeyed at the peak wave lengths of the complex species for the corresponding metal and complex ions. The molar absorbances of the metal ions were determined at pH = 1 and those of the complex species were obtained from the corresponding inflexion or saturation points in the ϵ_m v. pH curve (ϵ_m = optical density, D/total concentration m_t of metal in solution). If c_1 and c_2 are the concentrations of two species with molar absorbance ϵ_1 and ϵ_2 and Y_m and Y_t are the concentrations of metal-complexed and total EDTA present in solution, then,

$$D = \epsilon_1 c_1 + \epsilon_2 c_2 \tag{2}$$

$$m_t = c_1 + c_2 \tag{3}$$

$$\Sigma Y = Y_t - Y_m \tag{4}$$

The formation constant of MYH^- from M^{+2} and YH^{-3} was calculated using Equations (1), (2), (3) and (4).

(b) *Equilibrium constant for the formation of protonated, hydroxo and ammino complexes from the normal complex.* The equilibrium constants for the formation of the hydroxo and protonated complexes from the normal complex were calculated using the expression,

$$K^{MY}_{MYX} = \frac{(MYX^{(2+n)-})}{(MY^{2-})(X^{n-})} \tag{5}$$

where $X^n = H^+, OH^-, NH_3$. The concentrations of MY^{2-} and $MYX^{(2+n)-}$ were calculated using Equations (2) and (3), assuming that the metal is completely complexed. For calculating (OH^-), the ionic product of water was experimentally determined as $10^{-13.7}$. The ammino-complex was studied by the addition of known amounts of ammonium perchlorate and the free NH_3 concentration was calculated taking the equilibrium constant of the reaction, $NH_4^+ + OH^- = NH_3 + H_2O$ as 3.31×10^4 (8).

RESULTS AND DISCUSSION

1. *Copper*–EDTA *complexes*

The absorption peaks of copper (II) perchlorate at 206 and 800 mμ were shifted, on complex formation, to lower wave length regions and the molar absorption coefficients at both the peaks were enhanced. The molar absorption of the copper–EDTA solution was found to depend on the pH of the solution, as shown in Fig. 1,

---

* For calculations $\log K_2$ was taken as 2.76, an error of 0.1 log units in this value would affect the final $\log K^{MY}_{MYH}$ value by less than 1 per cent.

(7) A. E. MARTELL and F. F. CARINI, *J. Amer. Chem. Soc.* **74,** 5745 (1952).

(8) D. H. EVERETT and D. A. LANDSMAN, *Trans. Faraday Soc.* **50,** 1221 (1954).

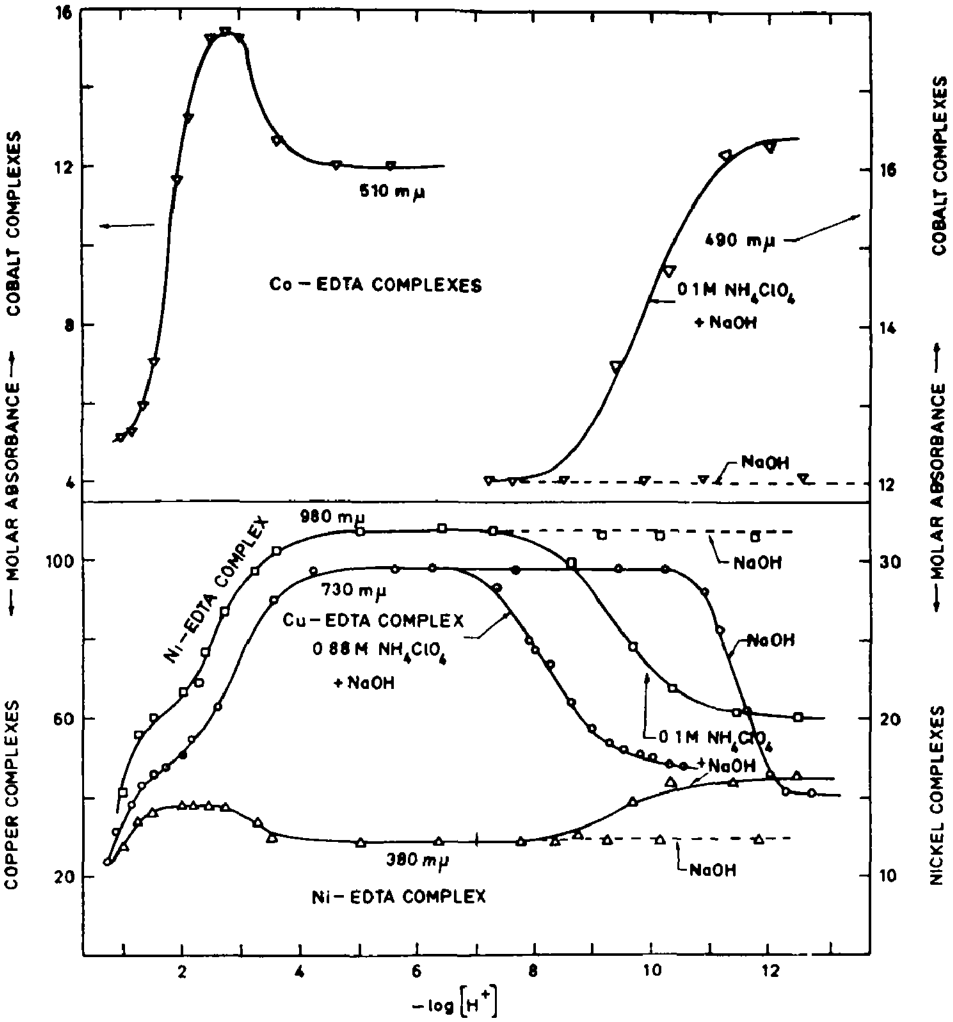


Fig. 1 - Variation of molar absorbances of Cu(II), Ni(II) and Co(II) EDTA solutions (1 1) as a function of H concentration Wavelengths 730 mμ for Cu, 980 mμ and 380 mμ for Ni, and 510 mμ (pH 0-6) and 490 mμ (pH 8-13) for Co-EDTA solutions

which indicates that (1) the normal complex is stable in the pH range 4-10 (2) at pH 10 hydroxo complex having lower absorption is formed (3) at pH < 3 5 protonated complex is formed which further decomposes at pH 1 5 to free copper and EDTA In the presence of NH$_4^+$ the reduction in ϵ_m begins at a lower pH ($\approx$ 6) where the formation of the hydroxo complex can be excluded This suggests the formation of ammino complex In Fig 2 are given the absorption spectra of normal (pH = 9), protonated (pH = 1 5), hydroxo (pH = 12 5) and ammino (0 88 NH$_4$ClO$_4$ and pH = 10 3) complexes of copper versenate The peak wave lengths and the corresponding ϵ_m values are given in Table 1 The stability constants of the different complexes, calculated at various pHs, are summarized in Table 2 The hydroxo complex was found to have an intense absorption peak at 206 mμ On continuous exposure to this frequency or to ultra-violet light the absorption was found to decrease gradually, the cause of this is being investigated

2 *Nickel*-EDTA *complexes*

The variation of ϵ_m with pH is shown in Fig 1 The hydroxo-complex was formed only at high OH concentrations, and precipitated on standing for a few days The absorption spectra of normal (pH - 6), protonated (pH = 1 9), ammino (0 1 M NH_4ClO_4 and pH 11 4) and hydroxo nickel-EDTA complexes are given in Fig 3

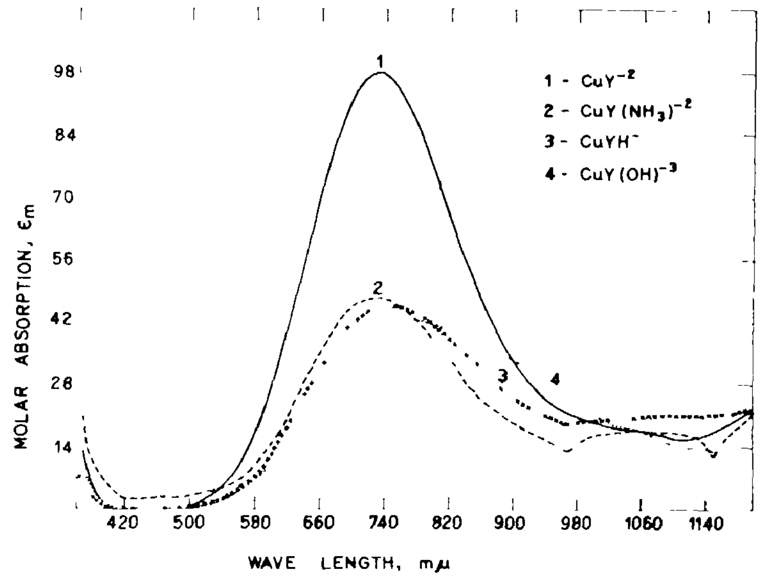


FIG 2 Molar absorbance of different Cu(II)-EDTA complex species 1—CuY^{2}, 2—CuY(NH$_3$)^{2}, 3—CuYH, 4—CuY(OH)$^{3-}$

It can be seen from Figs 1 and 3 that on complex formation the absorbance at 380 mμ is increased while that at 980 mμ is reduced The middle peak, at 590 mμ, remains almost unchanged except in the case of NiY NH$_3$, where it is slightly increased The formation constants of the different complexes were calculated using the 380 and 980 mμ peaks and the values are given in Table 2 (In the case of NiYH$^-$ only the 980 mμ peak was used since the variation in ϵ_m at 380 mμ was very small)

3 *Cobalt* (II)-EDTA *complexes*

The variation of ϵ_m with pH of the cobalt (II)-EDTA complexes were similar to those of nickel as can be seen in Fig 1 The hydroxo complex was formed only on addition of excess of sodium hydroxide, which on exposure to air for several days partly got precipitated and got oxidized to Co(III) The absorption spectra of the different complexes are given in Fig 4, from which it can be seen that in the case of protonated, hydroxo and ammino complexes there was appreciable displacement to the higher wavelength region and splitting of the 470 mμ peak

Due to wide variations in the experimental conditions a direct comparison of the stability constant data reported here with those of earlier workers cannot be made However, it may be mentioned that the average log K^{M}_{MYH} and log K^{MY}_{MYH} values given in Table 2 are of similar order of magnitude as those of SCHWARZENBACH *et al* (1)

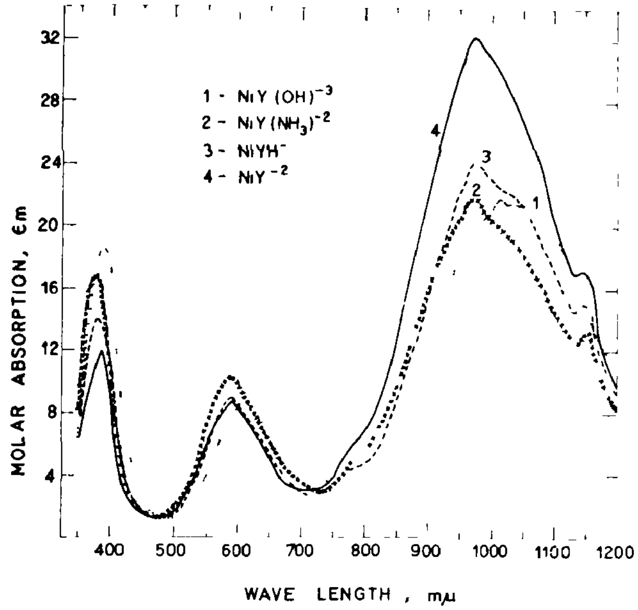


FIG 3—Absorption spectra of different Ni(II)-EDTA complexes 1—$NiY(OH)^{3}$, 2—$NiY(NH_3)^{--}$, 3—NiYH, 4—NiY^{2}

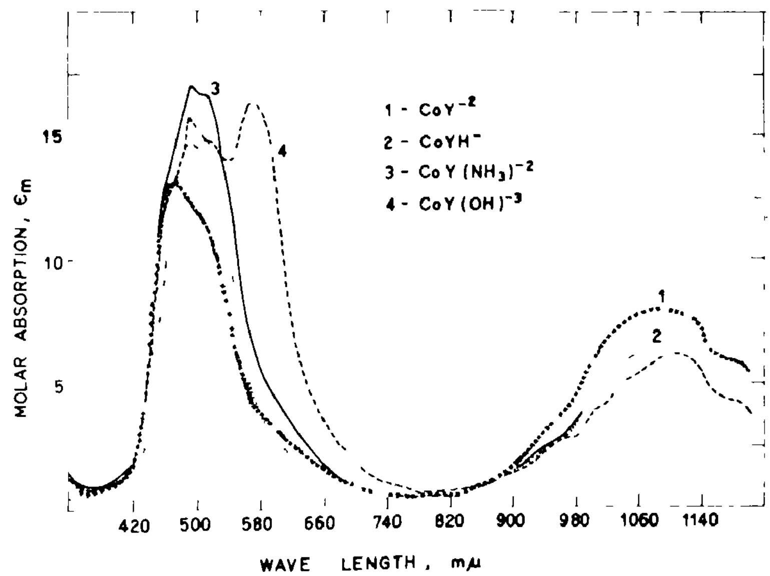


FIG 4—Absorption spectra of different Co(II) EDTA complexes 1—CoY^{2}, 2—CoYH, 3—$CoY(NH_3)^{2}$, 4—$CoY(OH)^{3}$